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Molecular characterization of polar organosulfates in secondary organic aerosol from isoprene and unsaturated aldehydes using liquid chromatography/(-)electrospray ionization mass spectrometry

Moleculaire karakterisering van polaire organosulfaten in secundair organisch aerosol van isopreen en onverzadigde aldehyden met behulp van vloeistofchromatografie/(-)elektrospray ionisatie massaspectrometrie

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List of abbreviations

(Note: only abbreviations are listed which have been used more than twice in the text)

AC	alternate current
AD	aerodynamic diameter
API	atmospheric pressure ionization
AS	ammonium sulfate
BC	black carbon
BIOSOL	Formation mechanisms, marker compounds, and source apportionment for BIOgenic atmospheric aerosOLS
BPC	base peak chromatogram
BVOC	biogenic volatile organic compound
DBAA	dibutylammonium acetate
DC	direct current
DNPH	2,4-dinitrophenylhydrazine
EC	elemental carbon
EI	electron ionization
EIC	extracted ion chromatogram
EPA	Environmental Protection Agency
ES	ethanesulfonate
ESI	electrospray ionization
EU	European Union
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GLV	green leaf volatile
GS	D-galactose-6-sulfate

Abbreviations

High-Vol	high-volume dichotomous virtual impactor
HILIC	hydrophilic interaction liquid chromatography
HPLC	high-performance liquid chromatography
IEPOX	isoprene epoxydiol
IP	ion-pairing
IPCC	Intergovernmental Panel for Climate Change
LC	liquid chromatography
MBO	2-methyl-3-buten-2-ol
<i>m</i> CPBA	<i>m</i> -chloroperoxybenzoic acid
MS	mass spectrometry
MSA	methanesulfonate
MW	molecular weight
<i>m/z</i>	mass-to-charge ratio
NL	normalization level
NMR	nuclear magnetic resonance (spectroscopy)
NO _x	mixture of NO and NO ₂
O ₂ ⁻	superoxide anion
OC	organic carbon
OM	organic matter
OS	organosulfate
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
POA	primary organic aerosol
PS	2-propanesulfonate
Q	quadrupole
RA	relative abundance

RF	radiative forcing / radio frequency
RH	relative humidity
ROS	reactive oxygen species
RP	reversed-phase
RT	retention time
SA	sulfuric acid
SIM	single ion monitoring
SOA	secondary organic aerosol
SRM	selected reaction monitoring
TOF	time-of-flight
TSP	total suspended particulates
u	unit of mass (in Dalton)
USA	United States of America
VOC	volatile organic compound
WHO	World Health Organization
WSOC	water-soluble organic carbon

CHAPTER 1

Introduction to atmospheric aerosols

1.1. Atmospheric aerosols

1.1.1. Definition and terms

An aerosol is a suspension of solid or liquid particles, or both, in the surrounding gas. In atmospheric aerosols, particles with an aerodynamic diameter (AD) smaller than 100 μm are also named particulate matter (PM), dust, mist, smoke, etc., although particulate matter is the preferred term.¹ As aerosol particles have an irregular shape, it is problematic to provide their diameter; therefore, the term “aerodynamic diameter” has been introduced for an irregular particle and is defined as the diameter of a spherical particle with a density of 1000 kg/m^3 and the same settling velocity as the irregular particle.²

According to the size of aerosol particles, they are divided in several sub-categories covering several orders of magnitude. All particles without considering their specific upper size are defined as total suspended particulates (TSP). Aerosol particles with AD less than 10 μm are defined as PM_{10} , while $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ refer to particles with AD smaller than 2.5 μm and between 2.5 and 10 μm , respectively. Coarse particles are particles with AD between 1 and 10 μm , while fine and ultrafine particles are those with AD smaller than 1 μm and 0.1 μm , respectively.³

1.1.2. Particle size distributions

Many properties of aerosols depend on their particle size; it is a key feature for understanding the behavior and effects of aerosols on health, visibility, and climate.

According to their size, aerosols can be roughly divided into several “modes”. The nucleation mode comprises aerosols with AD smaller than 10 nm, the Aitken mode particles with AD in the range of 10-100 nm, the accumulation mode particles with AD between 100 nm and 1 μm , and the coarse mode particles with AD larger than 1 μm . The aerosol number size distribution is dominated by

particles with AD smaller than 100 nm comprising of both nucleation and Aitken mode aerosols ($PM_{0.1}$), which are known as ultrafine aerosols. Due to their small size, they typically account only for a few percent of the total particulate mass. They can be formed by condensation of vapors during burning processes or by gas-to-particle conversion processes in the atmosphere (including nucleation).⁴ Accumulation mode particles are formed by condensation of vapors onto existing smaller particles (e.g., sulfates, nitrates, organics), by coagulation of nucleation mode particles, or are due to primary emissions (that is injected into the atmosphere in the particulate form).⁵ They are a substantial part of the aerosol mass and have a long atmospheric residence time. They are mainly eliminated from the atmosphere by rainout and washout. Coarse mode particles are formed by anthropogenic activities or by mechanical natural processes, such as wind action and erosion (mineral dust, sea salt, plant debris, pollen, etc.). Due to their higher mass, they have a short atmospheric lifetime and are easily removed by dry deposition.

Other concepts related to size distributions are: number size distribution (normally expressed as $dN/d\log D_p$ versus $\log D_p$, with N being the number concentration and D_p the particle diameter), surface area size distribution, and volume or mass size distribution (the latter expressed as $dM/d\log D_p$ versus $\log D_p$, where M is the mass concentration).

The size distributions of atmospheric aerosols are quite variable; they change with sampling site, time of the day, and season. They are affected by particle sources and composition, atmospheric conditions, topography, aging of the aerosol, and removal processes.⁶⁻¹⁰

Figure 1.1 provides a sketch of the number and mass size distributions of atmospheric aerosols. Despite the dominance of small size particles in terms of number, the contribution of ultrafine particles to the aerosol mass is very small.

The mass size distribution for an idealized urban aerosol and the fraction of the aerosol that is collected by a TSP sampler or samplers with PM_{10} or $PM_{2.5}$ inlets are illustrated in Figure 1.2. It can be noted that a minor fraction of the coarse mode aerosol is collected by a $PM_{2.5}$ sampler. It should be emphasized, though, that the minimum between the two modes is not always at the same diameter but varies with aerosol sources and source processes, and especially with relative humidity.

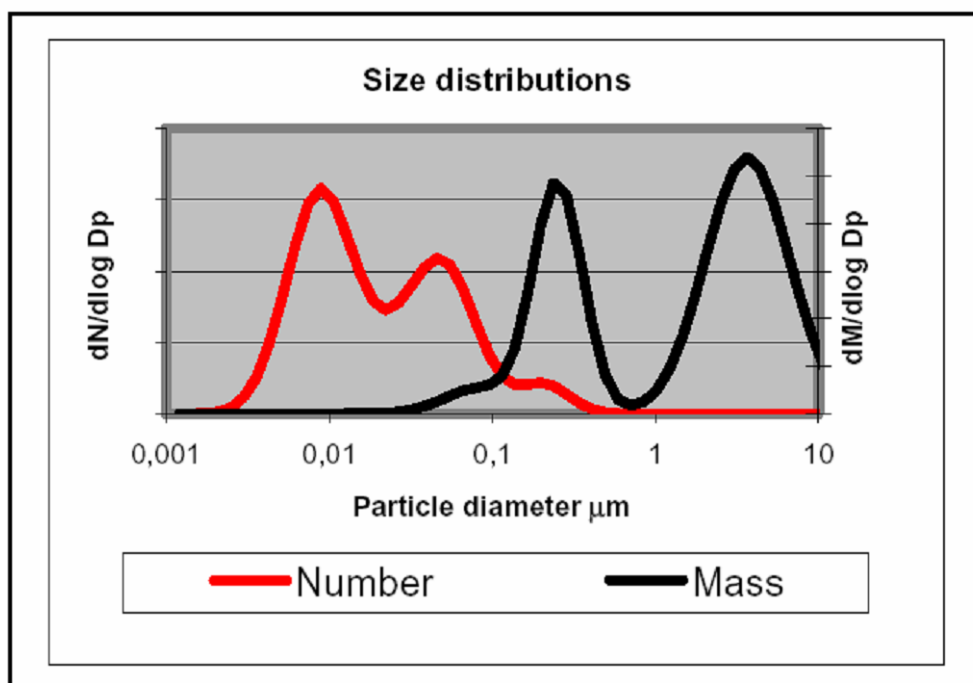


Figure 1.1. Sketch of the number and mass size distributions of the atmospheric aerosol.

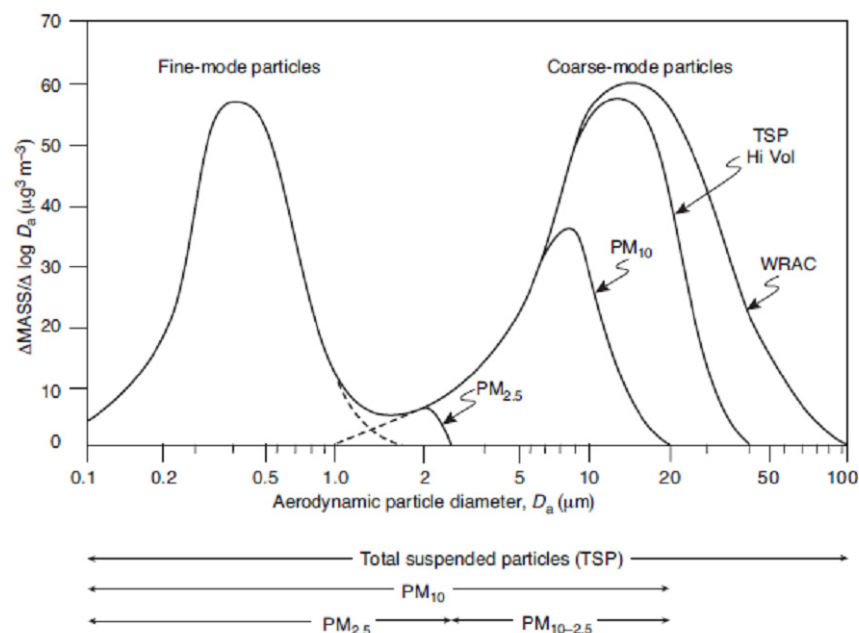


Figure 1.2. Mass size distribution for idealized urban aerosol and relationship with size fractions collected by samplers with different inlets. Abbreviation: WRAC, wide range aerosol collector. [taken from Wilson et al. (2011)]¹¹

1.1.3. Environmental fate of aerosols

Aerosols are removed from the atmosphere by two processes: dry and wet deposition. Water-soluble or hydrophilic particles with $AD > 80$ nm can act as cloud condensation nuclei, which form precipitation and on their way down to the Earth surface are scavenged and removed from the atmosphere. This process is called wet deposition and is the main mechanism of atmospheric removal. Particle deposition without the aid of precipitation is called dry deposition. Dry deposition is caused by gravitational sedimentation, convective transport, diffusion, or aerosol adhesion on the Earth's surface.

Aerosols in the accumulation mode have the longest residence time in the atmosphere due to their low-efficient removal from the atmosphere, which can vary from a few min to a few weeks, depending upon their size, injection altitude,

and proximity to precipitating cloud systems. As a consequence, aerosols can be found far from their source in the atmosphere, due to long-range transport.¹²⁻¹⁴

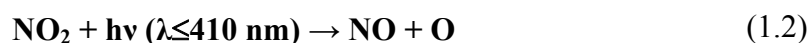
1.2. Atmospheric chemistry

1.2.1. Atmospheric oxidants

Whereas the major atmospheric constituents (N_2 , O_2 , Ar, CO_2) are (practically) unreactive with other atmospheric constituents, many atmospheric trace gases are quite reactive and play an important role in atmospheric chemistry. A very important class of reactive trace gas species are the atmospheric oxidants, i.e., the radicals ozone (O_3) and hydroxyl (HO^\bullet) [Note that although O_3 is a radical, it is not denoted as such within the atmospheric chemistry community; this is also the case for many other radical molecules (e.g., NO and NO_2)]. The formation of O_3 in the troposphere occurs through the following overall reaction:¹⁵



where NMHC denotes various reactive nonmethane hydrocarbons (ethylene, butane, etc.), the catalyst is NO_x ($\text{NO} + \text{NO}_2$) and $h\nu (\lambda \leq 410 \text{ nm})$ indicates a quantum of solar radiation of wavelength less than about 410 nm. Ozone formation by this mechanism is possible because solar radiation dissociates the NO_2 formed in Reaction (1.1):



and the recombination of O with molecular oxygen then produces ozone:



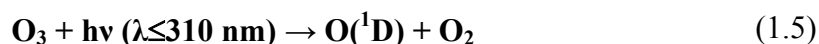
where M is a an atom or molecule (e.g., N_2 , O_2 or another gaseous species) which removes excess energy without otherwise participating in the reaction. Reactions (1.2) and (1.3) are two reactions in a chemical triad that links NO_x and O_3 . The third reaction of the group is:



These three rapid reactions establish a *photostationary state* among the concentrations of the principal reactants.

However, the cyclic nature of the reactions (1.2), (1.3) and (1.4) does not result in the net production of ozone (as can be seen by adding the reactants and products of the three reactions). Ozone production is only possible, as occurs in reaction (1.1), NO is converted to NO₂ by reacting with gases other than O₃ itself.

In 1971, a fundamental aspect of the atmosphere's reactivity was discovered by Hiram Levy, who pointed out that ozone photolysis by solar radiation at wavelengths shorter than about 310 nm leads to the production of the hydroxyl radical through the reactions:¹⁶



and:



where O(¹D) is the O atom in an excited singlet state, which is a more energetic state than the triplet ground state O(³P).

Levy's observation was crucial, because it was known that the hydroxyl radical was capable of reacting with a very large number of molecules. The exact role of hydrocarbons in reaction (1.1) was then revealed to be:



where R is the notation for any organic fragment consisting solely of carbon and hydrogen, such as CH₃, C₂H₅ or C₃H₇. This reaction is followed by:



and:



This bypassing of the ozone consumption reaction (1.4) enables nitric oxide (NO) to be oxidized to nitrogen dioxide (NO₂) without destroying ozone, the result

being sharply enhanced ozone concentrations when suitable amounts of both NO_x and NMHC are present. Since, according to reactions (1.1) and (1.2), also solar radiation is needed to produce O_3 , the concentration of O_3 depends on the intensity of solar radiation and follows the solar diurnal cycle.

1.2.2. Chemistry of organic species in the troposphere

The atmosphere is like a chemical reactor in which aerosols actively play a role by providing the media for gas-phase and particle-phase chemical reactions.

Due to the dynamic nature of the atmosphere and the variety of condensed matter and gaseous species that can participate in reactions, studying the real-time atmospheric gas-phase and particle-phase processes is a difficult task.¹⁷ Even though attempts have been made to study atmospheric chemistry using computer modeling, it is hard to connect an observed change to a specific process.¹⁸

The major process affecting the volatility of organic species is gas-phase oxidation, which results in species with sufficiently low vapor pressure to be condensable, leading mainly to the formation of secondary organic aerosol (SOA). Addition of different functional groups to the organics affects the polarity and consequently the vapor pressure of the organics.

The alkyl radicals, which are formed through the reaction of organic compounds with OH, NO_3 or ozone, react further with O_2 to form the RO_2 radical,³ as shown in reaction (1.8).

The subsequent chemistry is summarized in Figure 1.3.¹⁸ Further reaction of peroxy radicals with NO leads to the formation of alkoxy radicals or organic nitrate:



In a polluted environment where NO contributes to the formation of ozone, this reaction becomes significant. On the other hand, peroxy radicals can react with HO_2 to form hydroperoxides or lead to the formation of alcohols or carbonyls. In

addition, alkoxy radicals undergo unimolecular reactions such as decomposition and H-shift isomerization/ring closure, or react with O_2 . These reactions affect the volatility of the products and make them more condensable to qualify as SOA.

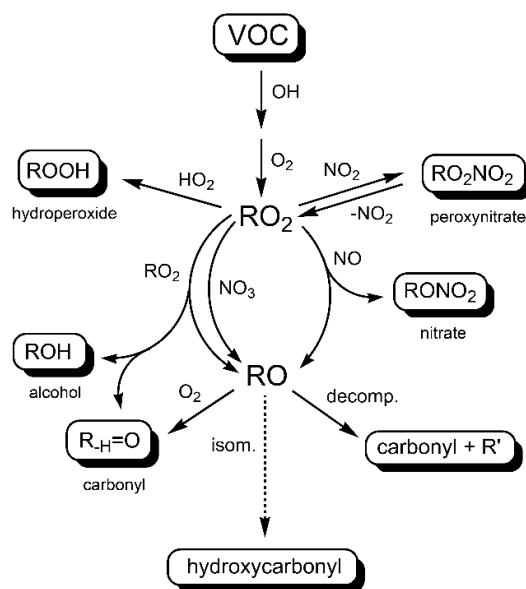


Figure 1.3. Simplified schematic of the OH-initiated degradation of volatile organic compounds to form first-generation products. [taken from Hallquist et al. (2009)]¹⁹

Another factor affecting chemical properties and SOA formation is chemical reaction of semi-volatile organics in the condensed or particle phase, including heterogeneous and multiphase reactions.¹⁷ Particle-phase reactions are significant only if they proceed on a timescale shorter than the lifetime of the aerosols. These reactions can proceed through non-oxidative processes (in which there is no change in the oxidation state of the total carbon) or oxidative (in which the carbon is oxidized).

Non-oxidative processes are associated with an increase in the molar mass of the parent volatile organic compounds (VOCs) through oligomerization or condensation reactions, which leads to a dramatic reduction in volatility, and can

occur both in the gas phase and the particle phase. Another type of non-oxidative processes that only recently have been recognized, occur in the particle phase, and lead to a reduction in volatility and an increase in polarity, are sulfation reactions, which are treated in detail in Section 2.3. Atmospheric oxidants (OH, NO₃, O₃, etc.), on the other hand, contribute to aging processes of SOA compounds through oxidative routes which despite the similarity in the chemical mechanism of the oxidation reactions with those of gas-phase reactions, may result in different reaction products. In addition, photolytic processes can potentially affect the oxidation state and volatility of SOA.²⁰

Furthermore, the aqueous medium is the predominant medium for particle-phase reactions, which can be modified by the presence of sulfuric acid in different stages of neutralization (e.g., with ammonia), nitric acid and nitrates, halogens (as ions), metals or water-soluble organic species, and can additionally provide media or substrates for chemical processes. Soot, sand (silicate) and sea-salt aerosols can provide reactive surfaces for various heterogeneous reactions.

1.3. Composition of atmospheric aerosols

Different chemical compounds (i.e., inorganic and organic compounds) can be identified in atmospheric aerosol mixtures, their composition depending on emission sources, physico-chemical processes, and temporal and spatial conditions. From an atmospheric, chemical and analytical standpoint, the aerosol compounds can generally be divided into several groups: (i) water-soluble inorganic salts; (ii) water-insoluble crustal matter; (iii) water-soluble organic compounds (WSOC), and (iv) water-insoluble organic compounds.

1.3.1. Inorganic compounds

Inorganic aerosols include anions (nitrate, sulfate, bromide, and chloride), cations (ammonium, alkaline, and earth alkaline metal cations), crustal material (silicon, aluminum and iron in mineral form which is practically water-insoluble), and

inorganic carbon such as carbonates. Major sources of inorganic compounds are: gas-to-particle conversion, anthropogenic emissions, bubble-bursting of seawater (sea spray), and air suspension of soil surfaces.^{21,22}

Sulfates can be primary (i.e., injected in the atmosphere in the particulate form) or secondary (i.e., resulting from gas-to-particle conversion). The bubble-bursting of seawater (sea spray) and volcanoes are sources of primary sulfate. Secondary sulfate results from anthropogenic activities through gas-to-particle and/or multiphase conversion processes of SO_2 , and also from the natural marine environment by oxidation of dimethyl sulfide emitted from phytoplankton.²³⁻²⁵ In the gas phase or liquid phase, SO_2 is oxidized to SO_3 and H_2SO_4 , then neutralized by NH_4^+ to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ aerosols.²⁶⁻²⁸ Ammonium is produced by gas-to-particle conversion of ammonia when it is neutralized with sulfuric acid or nitric acid. Secondary aerosols are also formed by photochemical oxidation of NO_x to HNO_3 , followed by neutralization to NH_4NO_3 , and by a large variety of reactions on anthropogenic VOCs.^{29,30}

Metal species such as Fe, Al, Ca, Mg, Na and K originate from mineral dust in the form of oxides, silicates and other minerals, while sea spray is a source for sodium, potassium, halides, magnesium, calcium and sulfates over the marine atmosphere. Furthermore, anthropogenic activities are the main source of elements like iron, copper, and lead.²⁸

1.3.2. Organic compounds

The carbonaceous fraction of atmospheric aerosols is a significant part of the total carbon content. A differentiation is made between elemental carbon (EC), organic carbon (OC), and inorganic carbon (mainly as carbonates), the latter being negligible in concentration in comparison to OC and EC.

EC has a chemical structure similar to graphite. It is primarily formed in the atmosphere during combustion processes, such as biomass, oil or coal burning,

and it is analyzed by a thermal method. One form of EC is called soot which is produced in a flame forming gaseous material (precursors). The term black carbon (BC) is often used to make a distinction between light-absorbing black-colored EC and the non-absorbing aerosol organic constituents. However, BC is not completely the same as EC. For example, light-absorbing soot (part of BC) does not only include graphite-like layered carbon (EC), but also organic molecules such as alkanes and polycyclic aromatic hydrocarbons (PAHs). Both BC and EC are fractions of the aerosol water-insoluble material.³¹

OC comprises the carbon which belongs to the aerosol organic components, and it constitutes the main part of carbonaceous aerosol in aerosol organic matter (OM). OC is divided into water-soluble OC (WSOC) and water-insoluble OC. Depending on its formation, OC contained in OM can be primary or secondary.³² OM represents up to 50% of the total aerosol mass.

1.3.2.1. Primary organic aerosol

Primary organic aerosol (POA) components are directly emitted into the atmosphere, often by dispersion processes from either natural or anthropogenic (man-made) sources, such as biomass and fossil fuel combustion, dust, plant abrasion, suspension of soil and microorganisms. They can be found in the particulate form or as semi-volatile vapors, which are condensable under normal atmospheric conditions.

Fossil fuel burning is one of the main anthropogenic sources for primary organic matter and is mainly connected to traffic. The type of engine (gasoline or diesel) as well as the possible treatment of the exhaust such as a catalyst can affect the composition of the exhaust-particles.³³⁻³⁵ Major compound classes are alkanes, alkanoic acids and PAHs, while hopanes and steranes are only minor compounds which are used as specific tracers for emissions of motor vehicles.

Another important anthropogenic source of primary PM is biomass burning because its contribution to the total aerosol mass is four times higher than that due to fossil fuel burning on the global scale.^{36,37} Anthropogenic biomass burning sharply increased from around 1750 and an increase of 50% was estimated from 1850 to 1990.^{38,39} Levoglucosan (1,6-anhydro- β -D-glucopyranose), an anhydro-sugar, is a general tracer for biomass burning. It is released by the thermal degradation of cellulose and hemicelluloses during the combustion process.⁴⁰ Moreover, other compounds such as alkanes, alkenes, alkanolic acids, di- and triterpenoids, monosaccharides, methoxyphenols and PAHs can be found in combustion aerosols.⁴¹

Industrial emissions are another source of primary OM which are mostly from power stations, iron and steel industries, incinerators, cement industry, refinery factories, etc.. Fly ash and heavy metals are released to the atmosphere by different industries which are responsible for a large fraction of the anthropogenic aerosol and have therefore been widely monitored and regulated. Consequently, in developed countries the emission of industrial dust aerosols has been reduced significantly, while in countries without a regulation for industrial emissions, the contribution of this source to the total aerosol mass might increase.²⁷

While the dispersion and mechanical disintegration processes at the surfaces of ocean and continent produce primary OM through the formation of sea-salt and soil dust particles, decomposition and dispersion of bulk plant material also produce aerosol particles, i.e., primary biogenic aerosol particles. Leaf debris, viruses, bacteria, spores and pollen, protozoa, algae and humic substances are biological sources of primary OM. Densely vegetated regions, particularly the moist tropics might have higher contribution to the formation of primary OM than in urban environments.^{14,42,43}

In summary, primary OM mainly contains:¹⁴

- 1) PAHs, alkanes, hopanes and alkanolic acids from gasoline and diesel combustion aerosols;
- 2) Anhydrosugars (i.e., levoglucosan, mannosan and galactosan from thermal decomposition of cellulose and hemicelluloses), methoxyphenols (guaiacols, syringols, anisoles from thermal decomposition of lignin), di- and triterpenoids, alkanes, alkanolic acids, PAHs and monosaccharides from biomass burning aerosols;
- 3) Plant epicuticular waxes (containing *n*-alkanes, *n*-alkanols, *n*-alkanals, fatty acids) from plant abrasion aerosols;
- 4) *n*-Alkanols, *n*-alkanes, *n*-alkanoic, *n*-alkenoic, alkanedioic and fatty acids, furans, acylglycerols, PAHs and cholesterol from aerosols generated by meat cooking operations; and
- 5) Sugars, sugar alcohols, lipids, proteins, humic material, cellulose and lignin from aerosols produced by suspension of soil, dust, spores, and microorganisms.

1.3.2.2. Secondary organic aerosol

OM makes up for around 50% of fine particles by mass in the Northern Hemisphere, with SOA contributing spatially between 65-95% of the OM.⁴⁴ Chemical reactions and gas-to-particle conversion of VOCs lead to the formation of SOA,¹⁴ which may proceed through different pathways: (i) gas-phase oxidation of VOCs that can either form new particles or condense onto pre-existing particles, (ii) heterogeneous reactions on particle surfaces, or (iii) in-cloud processing.⁴⁵ Volatile and semi-volatile alkanes, alkenes, aromatic hydrocarbons and oxygenated compounds are the main classes of SOA precursors.^{29,45}

Anthropogenic emissions mainly contain alkanes (~ 40%), alkenes (~10%) and aromatics (~20), with the rest being oxygenated and unidentified compounds.²⁹ Biogenic emissions are mostly alkenes, including isoprene, monoterpenes,

reactive VOCs, and unidentified VOCs.^{30,46} The reactive VOCs include sesquiterpenes, 2-methyl-3-butenol, and green leaf volatiles.^{30,46} SOA formation from terpenes and isoprene has attracted a lot of attention and is well studied, due to their huge emission rates on a global scale. The annual global natural VOC flux is estimated at 1150 Tg C, composed of 44% isoprene, 11% monoterpenes, 22.5% reactive VOCs, and 22.5% other VOCs.⁴⁶ It is estimated that biogenic VOC (BVOC) emissions exceed those of anthropogenic VOCs by one order of magnitude on a global scale.⁴⁶ Therefore, the contribution of organic compounds originating from the oxidation of naturally emitted VOCs to the global SOA mass is dominant.

Since the focus of this thesis is on the structural characterization of organosulfates derived from isoprene and the green leaf volatiles (GLVs), 2-*E*-hexenal and 3-*Z*-hexenal, and a related unsaturated C₅-aldehyde, 2-*E*-pentenal, an overview will be given about SOA formation from the latter BVOCs in Chapter 2 (Section 2.1.2). However, very important SOA precursors are monoterpenes, including α -pinene, β -pinene, *d*-limonene, and Δ^3 -carene [for reviews, see Hallquist et al. (2009); Nozière et al. (2015)].^{19,47}

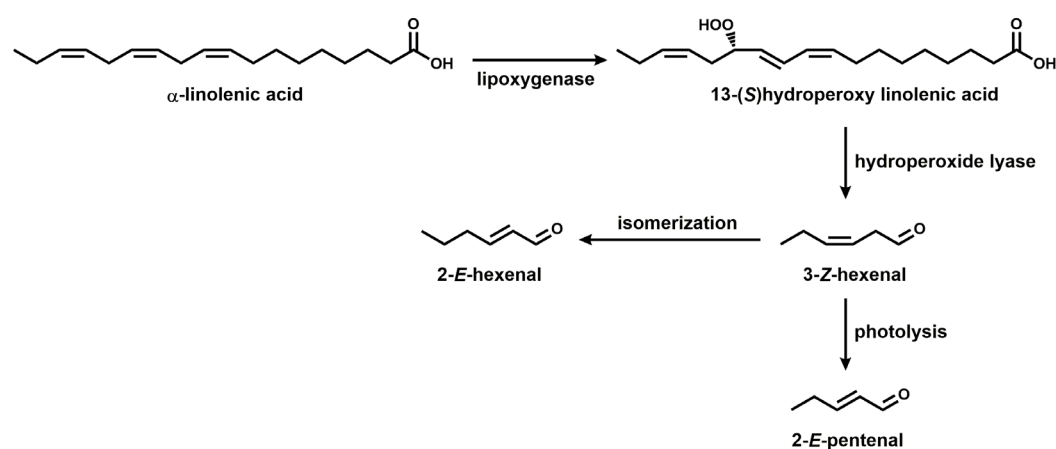
GLVs comprise unsaturated aldehydic C₆ compounds that are released by plants when they are wounded (e.g., grass cutting, animal grazing, storms) or attacked by insects [for reviews, see Holopainen et al. (2004) and Scala et al. (2013)].^{48,49} They are named after their specific “green” odor and play a crucial role in plant-plant and plant-insect communication. GLVs are biosynthesized in plant leaves from the unsaturated fatty acids, linoleic and α -linolenic acid, which are essential constituents of cell membrane lipids, by biochemical conversion with the enzymes lipoxygenase and hydroperoxide lyase.⁵⁰ One of the most abundant GLVs, 3-*Z*-hexenal, is formed from α -linolenic acid and it partly rearranges to 2-*E*-hexenal (Scheme 1.1). Both alkenals can be further metabolized by an alcohol

dehydrogenase and alcohol acyltransferase⁵¹ to the corresponding alcohols and their esters.⁵² The C₅-unsaturated aldehyde, 2-*E*-pental, is a known photolysis product of 3-*Z*-hexenal (Scheme 1.1).⁵³

Marine biogenic emissions are another important natural source of secondary OM. Dimethylsulfide gas is emitted by phytoplankton species during their life cycle, can undergo radical-initiated oxidation in the gas phase and lead to the formation of SO₂, which subsequently is oxidized to non-sea-salt sulfate and to particulate-phase methanesulfonic acid.^{23,24,28,54,55}

Not only primary OM is emitted due to the human activities, but also gaseous precursors of secondary inorganic aerosol and SOA (e.g., SO₂, NO_x, and VOCs).

The most important anthropogenic VOCs emitted into the atmosphere are aromatic hydrocarbons. Field and laboratory studies including chamber experiments led to the identification of aromatic hydrocarbon-related products.⁵⁶



Scheme 1.1. Summary of the formation of the unsaturated aldehydes 3-*Z*-hexenal and 2-*E*-hexenal in plant leaves through the lipoxygenase/hydroperoxidase lyase pathway, and subsequent photolysis of 3-*Z*-hexenal to 2-*E*-pental.

Three groups can be identified as products of the oxidation of aromatic hydrocarbons: (i) ring-retaining aromatics, (ii) ring-retaining non-aromatics, and (iii) ring-degradation products.¹⁹ Ring-retaining aromatic products that are rather stable can originate from the OH-addition to the aromatic ring, a process that

leads to the formation of OH- and NO₂-substituted rings, or from the H-atom abstraction of alkyl substituents (toluene, xylenes, etc.) forming, for example, aromatic aldehydes or carboxylic acids. On the other hand, ring-retaining non-aromatic products are unstable and are readily oxidized by ozone or nitrate radicals. Therefore, their concentration in atmospheric aerosols is negligible. Ring-degradation products comprise short-chain carboxylic and dicarboxylic acids, such as succinic, pyruvic, malonic, maleic, methylmaleic, malic, glyoxylic, and oxalic acid. However, these products can also be secondary products of other precursors which are released from biomass burning or fossil fuel combustion, or can be due to further degradation of higher-molecular weight (MW) dicarboxylic acids.^{32,57}

1.4. Impacts of aerosols

1.4.1. Impacts of aerosols on air quality

Already in the Middle Ages, wood and coal burning has been known to cause severe smog episodes in cities such as London.⁴³ The Industrial Revolution led to a large increase in coal burning, severely worsening air pollution. The London-type smog is characterized by an accumulation of fuel burning particles (such as soot) and vapors (such as SO₂) in an inversion layer. The dense haze impairs visibility, blackens or corrodes buildings, and irritates the eyes and lungs.⁴³ Besides the chronic exposure, pollution events caused acute spikes in mortality. During the Great Smog event in London in the winter of 1952 to 1953, an estimated 12,000 deaths were related to the pollution.

Besides this London-type smog, a different type of air pollution is the so-called photochemical smog, which involves the photochemical processing of primary particulate and gaseous emissions. In Los Angeles, for example, almost daily smog episodes could be observed from the start of the twentieth century on, which increased in severity with the increase in automobile traffic.⁴³ In the 50s it was

discovered that such episodes are caused by the photochemical processing of a mixture of emitted hydrocarbons and nitrogen oxides. Under sunlight, strong ozone formation takes place, accompanied by the formation of organic peroxides, which cause eye irritation and crop damage.¹⁷ Aerosol formation was also observed, and found to reduce visibility.

Since the 80s/90s, as health effects became better understood, increasingly strict government controls on airborne particulate matter were implemented and verified through measurement networks in the European Union (EU) and the United States of America (USA). First PM_{10} , and more recently $\text{PM}_{2.5}$ limits have been enforced. For example, in the EU, PM_{10} should not exceed a 24-hour average of $50 \mu\text{g m}^{-3}$ for more than 35 days.⁵⁸ Related pollution control measures have led to a decrease of air pollution in the USA and Europe.

A recent study carried out in Flanders, where we are struggling to meet the PM_{10} limits, concluded that more stringent regulations on wood burning, in particular in winter, could help in complying with the European air quality legislation.⁵⁹ This conclusion was based on the fact that about 10% of the PM_{10} mass is due to wood burning in winter.

1.4.2. Health impacts of aerosols

Both short- and long-term exposure to fine particulate matter has a significant detrimental impact on health, as has been shown by a large number of population studies.⁶⁰ Such studies find significant correlations between PM_{10} or $\text{PM}_{2.5}$ and increased hospital admissions or mortality. For long-term exposure, a $10 \mu\text{g m}^{-3}$ decrease of $\text{PM}_{2.5}$ was shown to lead to a 7.3 (± 2.4) month increase in life expectancy.⁶⁰ Such estimates of the health impact of PM have been combined with global PM models to estimate the global mortality due to anthropogenic PM. The World Health Organization (WHO) reports that ambient air pollution contributed to about 3.7 million excess deaths globally during 2012.⁶¹

Additionally, indoor pollution due to indoor fuel burning, mostly in developing nations, contributes to about 4.3 million deaths per year.⁶² Together, air pollution is a contributing factor in about one in eight deaths worldwide.

Toxicological studies have shed light on the mechanisms behind these adverse health effects. The smallest particles penetrate deepest into the lung, reaching the alveoli.⁶³ Diesel engine exhaust (consisting of black and organic carbon) can cause inflammation of airways and reduce vascular function and cause myocardial ischaemia, while also mutagenic effects (potentially leading to cancer) have been reported.⁶¹ PM has been shown to enhance plaque formation in arteries.⁶⁴

Various studies support the hypothesis that PM_{2.5} toxicity is caused by the generation of reactive oxygen species (ROS) in lung cells.⁶⁵⁻⁶⁷ ROS are oxygen-containing compounds, including superoxide anion (O₂⁻), hydrogen peroxide (H₂O₂), and hydroxyl radical (OH), shown to act as powerful oxidants *in vivo* and *in vitro*, causing cell damage referred to collectively as oxidative stress.⁶⁸ The prevailing view of the mode of action specific to PM_{2.5} is interaction with the airway epithelial cells and macrophages to generate ROS,⁶⁹ triggering a cascade of events associated with inflammation and apoptosis. A commonly used method to quantify redox activity of a PM_{2.5} sample and its potential to generate ROS is the dithiothreitol assay.⁷⁰

The oxidizing potential of PM from diesel exhaust, diesel exhaust with ozone, and PAHs has been investigated,⁷¹ but very little is known about the toxicity of biogenic SOA. A very recent study examined the toxicity of isoprene SOA, comprising organosulfates.⁷² The potential of this material to generate ROS was assessed using the dithiothreitol assay. Very relevant outcomes are that the toxicity of 2-methylglyceric acid, a SOA product derived from methacrolein and methacrylic acid epoxide, formed under high-NO_x conditions, is higher than that from isoprene epoxydiols and 2-methyltetrols, formed at low-NO_x, and that the

toxicity of methacrolein and methacrylic acid epoxide SOA is comparable to that of diesel exhaust. The atmospheric abundance of isoprene SOA and the enhanced yields on mixing with anthropogenic pollutants warrants further study of responses of biological systems to define potential health risks posed by exposure to this ubiquitous PM.

1.4.3. Climate change and impacts of aerosols

The global average temperature has increased by about 0.85 °C over the period 1880 to 2012, most probably due to anthropogenic forcings, including emissions of CO₂, methane, halocarbons, and aerosols.⁷³

The effect of aerosols on climate can be divided into a direct effect, through scattering or absorption of sunlight, and an indirect effect, through the role of aerosols on clouds (e.g., condensation nuclei).³ By scattering and reflecting light, aerosols have a cooling effect, because they reflect part of the incoming sunlight back into space. However, aerosols also absorb part of the incoming sunlight. Black carbon is a strong absorber, and therefore contributes to global warming, while SOA and most of the inorganic aerosol are generally much weaker absorbers. The indirect effect is more complex, and is caused by the ability of aerosol particles to serve as cloud seeds. Higher cloud condensation nuclei numbers lead to clouds with a higher cloud droplet density, which have a higher albedo (that is reflectivity of light), and therefore cool the atmosphere more effectively. There is also an effect on cloud lifetime. The effect of aerosols and gases on climate is denoted as radiative forcing (RF). RF is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system and is an index of the importance of the factor as a potential climate change mechanism. Within the Intergovernmental Panel for Climate Change (IPCC)⁷³ radiative forcing values are for changes relative to

preindustrial conditions defined at 1750 and are expressed in Watts per square meter (W/m^2).

Anthropogenic aerosols have a direct RF for which current estimates range from $+0.23 \text{ W/m}^2$ to -0.77 W/m^2 , and an indirect RF between -0.06 W/m^2 and -1.33 W/m^2 (Figure 1.4). Aerosols contribute the largest part of the uncertainty on the total anthropogenic radiative forcing estimate.⁷³

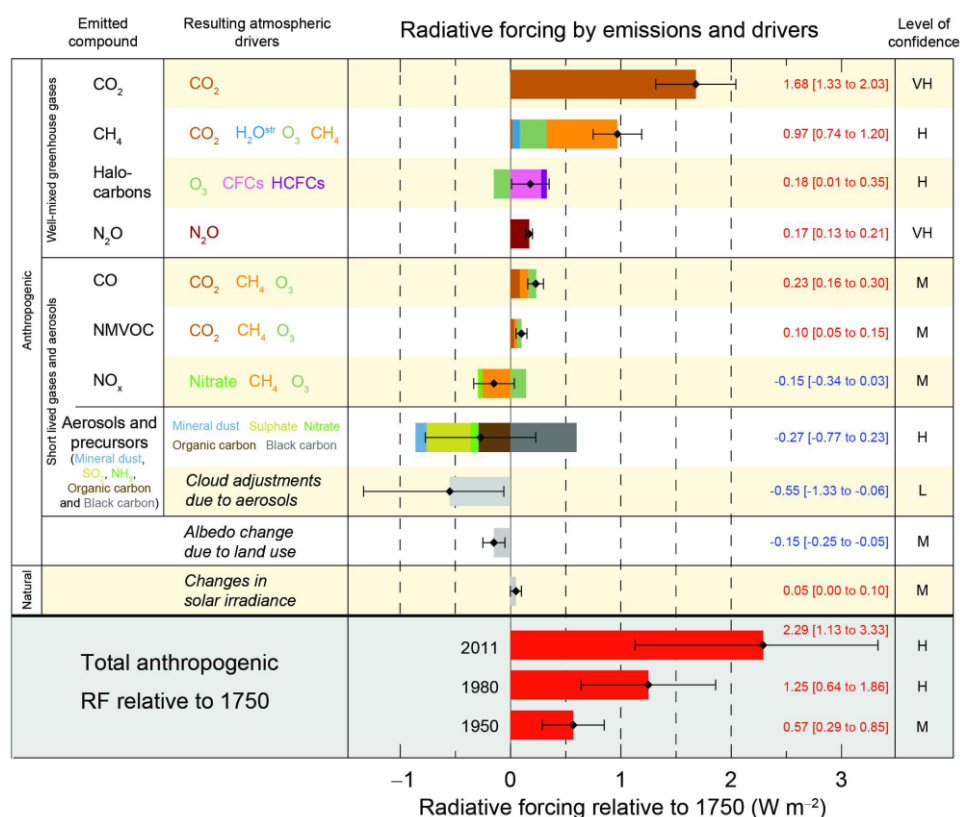


Figure 1.4. Radiative forcing estimates in 2011 relative to 1750 and aggregated uncertainties for the main drivers of climate change. Values are global average radiative forcing (RF), partitioned according to the emitted compounds or processes that result in a combination of drivers. The best estimates of the net radiative forcing are shown as black diamonds with corresponding uncertainty intervals; the numerical values are provided on the right of the figure, together with the confidence level in the net forcing (VH very high, H high, M medium, L low, VL very low) [Note that “confidence”, as defined in the IPCC reports, should not be interpreted probabilistically; it is distinct from ‘statistical confidence’]. Albedo forcing due to black carbon on snow and ice is included in the black carbon aerosol bar. Concentration-based RFs for gases can be obtained by summing the like-colored bars. Total anthropogenic radiative forcing is provided for three different years relative to 1750. [this is Figure SPM.5 from IPCC, Working Group I (2013)]⁷³

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CHAPTER 2

Objectives and background

2.1. Motivations and organization of this thesis

The objectives of this work were to characterize SOA markers of the organosulfate type at the molecular level in ambient fine aerosol using mass spectrometric approaches. More specifically, the focus is on the molecular characterization of polar organosulfates that originate from the oxidation of isoprene and the unsaturated aldehydes, 2-*E*-pentenal, 2-*E*-hexenal, and 3-*Z*-hexenal. While organosulfates related to isoprene SOA have been studied by several research groups, organosulfates related to the latter unsaturated aldehydes, which belong to the group of the green leaf volatiles, had not been studied yet before the start of this doctoral research. Polar organosulfates derived from isoprene and unsaturated C₅ and C₆ aldehydes are of climatic interest because they contribute to the hydrophilic properties of aerosols, increasing their capacity to act as cloud condensation nuclei.¹⁻⁴ In addition, organosulfates are potential marker compounds for SOA formation occurring under acidic conditions by particle-phase reactions with sulfuric acid,⁵ formed by oxidation of sulfur dioxide, which is mainly from anthropogenic origin in continental regions of the globe.⁶ Furthermore, they contribute to PM acidity because of the presence of a sulfate group.

For reaching the objectives, two types of samples were used: laboratory-generated SOA samples obtained through international collaboration with the National Exposure Laboratory of the US Environmental Protection Agency (EPA) and archived ambient PM_{2.5}, collected from K-pusztá, Hungary. The samples were analyzed by liquid chromatography (LC)/electrospray ionization (ESI)-mass spectrometry (MS), making use of tandem and high-resolution MS, and the MS data were interpreted in detail.

The research carried out within the frame of this thesis is presented in Chapters 4, 5, 6, and 7. Information about instrumentation and methods is provided in Chapter

3. The background related to organosulfate formation and analytical methodology that are relevant to the performed research is presented in the following sections of this Chapter.

2.2. SOA formation: background

2.2.1. SOA formation from isoprene

For a long time, isoprene was assumed not to be a precursor for SOA but only to result in volatile oxidation products such as methacrolein and methyl vinyl ketone. However, it is now well established that isoprene is a precursor for SOA. The discovery of the 2-methyltetrols in 2004 by Claeys and co-workers stimulated many research groups studying SOA formation to re-evaluate SOA formation from isoprene.⁷ During the past decade substantial progress has been made with the structural elucidation of major isoprene SOA products, called markers or tracers, which can be used for source identification. A compilation of isoprene SOA markers and selected references about their structural characterization are given in Table 2.1.

The major SOA markers formed under low-NO_x conditions involving gas-phase reactions with the OH radical include the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, and C₅-alkene triols.^{8,9} Their formation mechanism as well as that of the 2-methyltetrol-related sulfate esters is summarized Scheme 2.1. Their gas-phase intermediates are C₅-epoxydiols (IEPOX), which occur in two forms, β- and δ-IEPOX.^{10,11} A major SOA product generated under both low- and high-NO_x conditions is 2-methylglyceric acid.¹² Different formation pathways have been reported for the latter product. A first pathway involves reactive uptake of methacrolein in the aqueous phase (or a hydrophilic particle) and subsequent oxidation with hydrogen peroxide.¹² A second route is a high-NO_x pathway, involving methacrylic acid epoxide, formed by decomposition of methacryloylperoxynitrate, a gas-phase intermediate.¹⁰

Table 2.1. Overview of isoprene SOA markers and selected references on their structural characterization. Only markers are listed that are found at significant concentrations in ambient fine aerosol ($> 1 \text{ ng m}^{-3}$). [taken from Nozière et al. (2015)]¹³

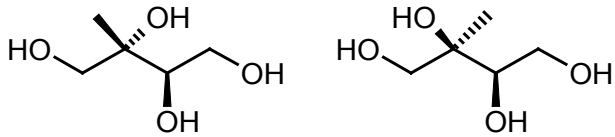
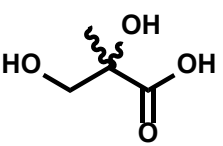
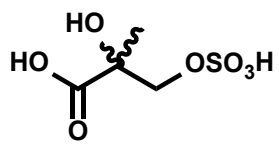
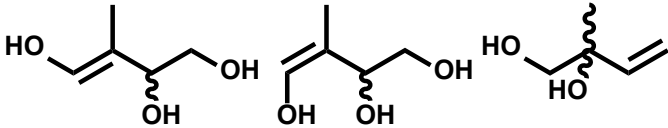
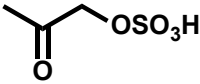
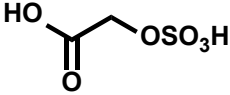
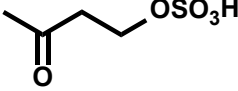
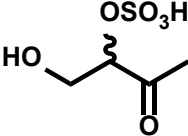
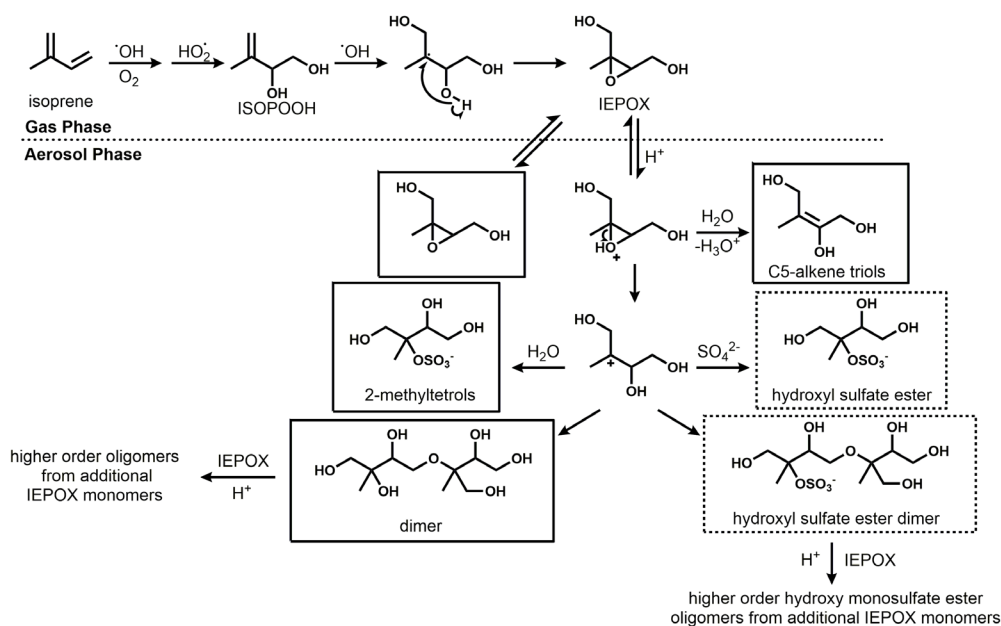
Chemical structure and name (MW)	Selected references
<p>2-methyltetrols (MW 136) (1,2,3-tetrahydroxy-2-methylbutane)</p>  <p>2-methylthreitol (2R,3R) 2-methylerythritol (2S,3R) + 2S,3R isomer +2R,3S isomer</p> <p>2-methyltetrol derivatives</p> <p>2-methyltetrol organosulfates (MW 216)</p> <p>2-methyltetrol nitrooxy organosulfates (MW 261)</p> <p>2-methyltetrol dinitroxy organosulfates (MW 306)</p>	<p>⁷ Claeys et al. (2004) ¹⁴ Wang et al. (2004) ⁹ Surratt et al. (2006)</p> <p>⁵ Surratt et al. (2007) ¹⁵ Gómez-González et al. (2008) ¹ Surratt et al. (2008)</p>
<p>2-methylglyceric acid (MW 120) (2,3-dihydroxy-2-methylpropanoic acid)</p> 	<p>¹² Claeys et al. (2004) ⁹ Surratt et al. (2006) ¹⁶ Szmigielski et al. (2007)</p>
<p>3-sulfooxy-2-hydroxy-2-methylpropanoic acid (MW 200)</p> 	<p>¹⁵ Gómez-González et al. (2008)</p>

Table 2.1. continued

Chemical structure and name (MW)	Selected references
<p>C₅-alkene triols (MW 118)</p> 	<p>¹⁷ Wang et al. (2005)</p> <p>⁹ Surratt et al. (2006)</p>
<p>polar organosulfates related to methacrolein or methyl vinyl ketone</p> <div style="display: flex; justify-content: space-around;"> <div> <p>sulfooxy acetone (MW 154)</p>  </div> <div> <p>sulfooxy acetic acid (MW 156)</p>  </div> </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div> <p>1-sulfooxybutane-3-one (MW 168)</p>  </div> <div> <p>2-sulfooxy-3-hydroxybutan-2-one (MW 184)</p>  </div> </div>	<p>² Olson et al. (2011)</p> <p>¹⁸ Schindelka et al. (2013)</p> <p>¹⁹ Shalamzari et al. (2013)</p>



Scheme 2.1. Proposed pathway for the formation of isoprene SOA markers, including 2-methyltetrols, C₅-alkene triols and dimers, and corresponding sulfate esters, through acid-catalyzed reactions of the gas-phase intermediate IEPOX. [taken from Surratt et al. (2010)]⁸

2.2.2. SOA formation from the unsaturated aldehydes 2-*E*-pentenal, 2-*E*-hexenal, and 3-*Z*-hexenal

Unlike for isoprene and major monoterpenes, SOA formation from unsaturated aldehydes, including the green leaf volatiles 2-*E*-hexenal and 3-*Z*-hexenal, has, to our knowledge, not been explored by research groups other than ours. However, there is emerging evidence that GLVs serve as precursors for SOA.^{15,20-22}

A compilation of markers for SOA from 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal, and selected references about their structural characterization, based on literature data and the work carried out in the frame of this doctoral thesis, are given in Table 2.2. For further information on possible formation mechanisms, reference is made to Chapters 6 and 7 of this thesis.

Table 2.2. Overview of markers for SOA from 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal, and selected references on their structural characterization.

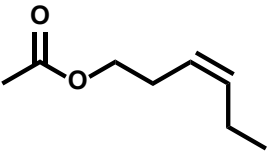
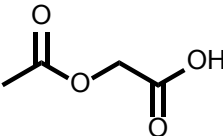
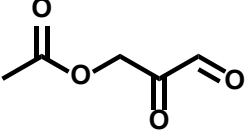
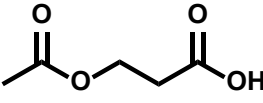
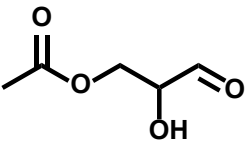
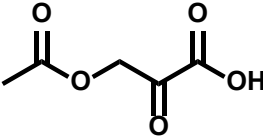
Chemical structure and name (MW)	Selected references
<p>Markers related to 3-<i>Z</i>-hexenyl acetate (MW 142)</p>  <p>3-<i>Z</i>-hexenyl acetate derivatives</p> <p>2-acetoxyacetic acid (MW 118)</p>  <p>2,3-dioxopropyl acetate (MW 130)</p>  <p>3-acetoxypropanoic acid (MW 132)</p>  <p>2-hydroxy-3-oxopropyl acetate (MW 132)</p> 	<p>²⁰ Jain et al. (2014)</p> <p>²¹ Hamilton et al. (2009)</p>
<p>3-acetoxy-2-oxopropanoic acid (MW 146)</p> 	<p>²¹ Hamilton et al. (2009)</p>

Table 2.2. continued

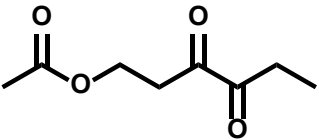
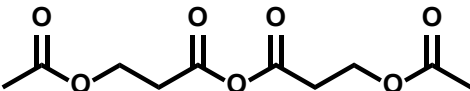
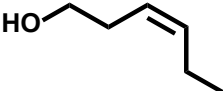
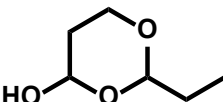
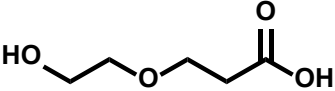
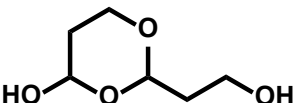
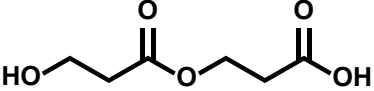
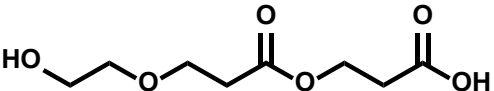
Chemical structure and name (MW)	Selected references
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<p>Markers related to 3-Z-hexen-1-ol (MW 100)</p>  <p>3-Z-hexen-1-ol derivatives</p> <p>2-ethyl-1,3-dioxan-4-ol (MW 132)</p>  <p>3-(2-hydroxyethoxy)propanoic acid (MW 134)</p>  <p>2-(2-hydroxyethyl)-1,3-dioxan-4-ol (MW 148)</p>  <p>3-(3-hydroxypropanoyloxy)propanoic acid (MW 162)</p>  <p>3-(3-(2-hydroxyethoxy)propanoyloxy)propanoic acid (MW 206)</p> 	<p>²¹ Hamilton et al. (2009)</p>

Table 2.2. continued

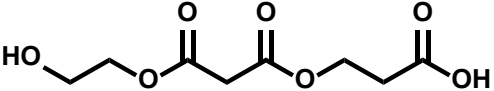
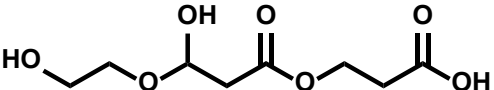
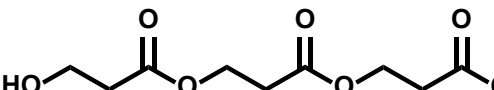
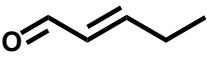
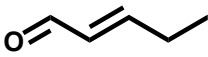
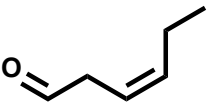
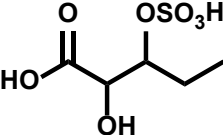
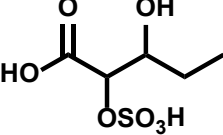
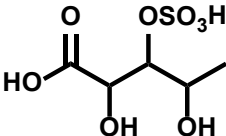
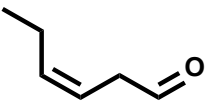
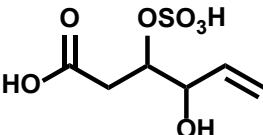
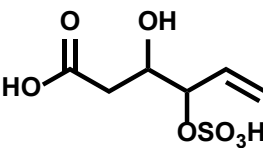
Chemical structure and name (MW)	Selected references
<p>3-(3-(2-hydroxyethoxy)-3-oxopropanoyloxy)propanoic acid (MW 220)</p>  <p>3-(3-hydroxy-3-(2-hydroxyethoxy)propanoyloxy)propanoic acid (MW 222)</p>  <p>3-(3-(3-hydroxypropanoyloxy)propanoyloxy)propanoic acid (MW 234)</p> 	<p>²¹ Hamilton et al. (2009)</p>
<p>Markers related to 2-<i>E</i>-pentenal (MW 84), 2-<i>E</i>-hexenal (MW 98), and 3-<i>E</i>-hexenal (MW 98)</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>2-<i>E</i>-pentenal</p> </div> <div style="text-align: center;">  <p>2-<i>E</i>-hexenal</p> </div> <div style="text-align: center;">  <p>3-<i>Z</i>-hexenal</p> </div> </div> <p>3-sulfooxy-2-hydroxypentanoic acid (MW 214)</p>  <p>2-sulfooxy-3-hydroxypentanoic acid (MW 214)</p> 	<p>¹⁵ Gómez-González et al. (2008) and this work</p>

Table 2.2. continued

Chemical structure and name (MW)	Selected references
3-sulfooxy-2,4-dihydroxypentanoic acid (MW 230) 	
Markers related to 3-Z-hexenal (MW 84)  3-sulfooxy-4-hydroxyhex-5-enoic acid (MW 226)  4-sulfooxy-3-hydroxyhex-5-enoic acid (MW 226) 	²² Shalamzari et al. (2014)

2.3. Organosulfates

2.3.1. Occurrence and origin of organosulfates

It has been suggested that organosulfates (OSs) are a significant component of fine OM.^{1,5,23-25} For fine aerosol from K-pushta, Hungary, collected during summer, for example, the organosulfate fraction was estimated to be as high as 30% of the total organic mass and to correspond to 6-12% of the bulk sulfur mass.^{1,26}

Laboratory chamber experiments have demonstrated that SOA formed from BVOCs [i.e., isoprene, 2-methyl-3-buten-2-ol (MBO), monoterpenes, and sesquiterpenes)] in the presence of oxidants and sulfuric acid, contain a large

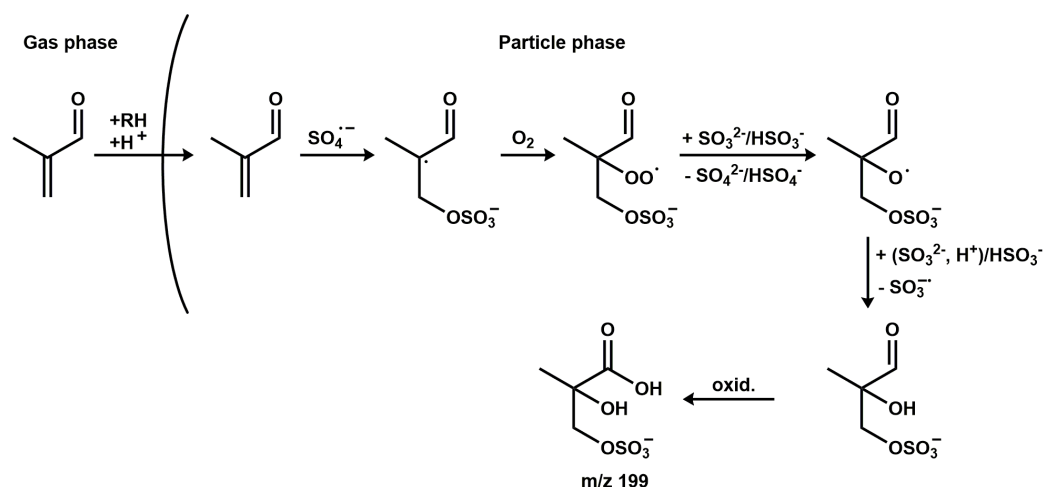
organosulfate component.^{5,27-29} Organosulfates have been detected in rural, urban and marine aerosols,³⁰ cloud water,³¹ and rain water.^{1,5,15,29,30,32-35}

Of particular interest for this doctoral work are the organosulfates related to isoprene, including those derived from IEPOX, methacrolein, and methyl vinyl ketone (Table 2.1). Several mechanisms have been reported that lead to the formation of organosulfates. A first well-established mechanism is the reactive uptake of epoxy-containing compounds and reaction with sulfuric acid in the particle phase. This mechanism accounts for the formation of the 2-methyltetrol sulfate esters from β - and δ -IEPOX.⁸ A second mechanism is the reactive uptake of an unsaturated compound such as methacrolein in the particle phase and subsequent reaction with the sulfate radical anion (Scheme 2.2). However, the first mechanism only can explain the formation of 2-methyltetrol sulfate esters under low-NO_x conditions but not at high-NO_x. Insights have recently been gained about their formation and that of the 2-methyltetrols in the free form under high-NO_x conditions, where the oxidation of isoprene with OH radicals partly results in the formation of organonitrates, which subsequently partition to the particle phase and can undergo a nucleophilic substitution with water or sulfate in the case of a tertiary nitrate group.^{36,37}

Isoprene SOA-related organosulfates that have recently been structurally elucidated and detected in ambient fine aerosol include sulfate esters of 3,4-dihydroxybutan-2-one, glycolic acid, 1-hydroxy-3-oxobutane, and hydroxyacetone (Table 2.1).^{2,18,19,38,39} Their formation has, as that of the sulfate ester of 2-methylglyceric acid, been explained by multiphase reactions involving the sulfate radical anion.^{2,18,29,39-41} Furthermore, the formation of the sulfate ester of 2-methylglyceric acid from methacrolein has also been explained through methacroylperoxynitrate and further decomposition to methacrylic acid epoxide.⁸

A precursor for biogenic SOA that is related to isoprene and is worth mentioning is 2-methyl-3-buten-2-ol. MBO is an important BVOC emitted from pine trees and was found to lead to the formation of OSs accounting for 0.25% of the OM in the Manitou Forest Observatory in Colorado.²⁹ The major MBO-derived OS that can serve as a tracer for MBO SOA is the sulfate ester of 1,2,3-trihydroxy-3-methylbutane, an analog of the 2-methyltetrols.²⁹ Organosulfates identified in marine aerosols with a pure biogenic origin (also the sulfate group) include sulfate esters of C₉₋₁₃ hydroxycarboxylic acids, which likely originate from the oxidative degradation of algal unsaturated lipids.³⁰ Furthermore, aromatic organosulfates originating from anthropogenic VOCs have been reported. These organosulfates include benzylsulfate, phenylsulfate, and methyl- and dimethylphenylsulfate; of these, benzylsulfate was detected at significant concentrations (range 50 pg – 500 pg m⁻³) in Lahore, Pakistan.^{42,43}

Despite extensive research during the last decade on the chemical characterization and formation of organosulfates, there are still a number of knowledge gaps, such as unknown precursors and mechanisms. With regard to unknown precursors, evidence is provided in the present thesis that unsaturated aldehydes belonging to the group of the green leaf volatiles serve as precursors for polar organosulfates.



Scheme 2.2. Formation of organosulfates from methacrolein through reactive uptake in the particle phase and reaction with the sulfate radical anion. [adapted from Rudzinski et al. (2009)]⁴⁰

2.3.2. Analytical techniques for organosulfates

For an up-to-date review on analysis methods for the molecular characterization of organic compounds in the atmosphere, see the recent review by Nozière et al. (2015).¹³ In this section, only techniques will be covered that are suited to the molecular characterization of organosulfates, including off-line and on-line techniques.

2.3.2.1. Off-line techniques

2.3.2.1.1. Generalities

Off-line analytical methodology is the most traditional way of studying aerosol composition, which has developed considerably over the past decades. In particular, there is a current concern about the molecular characterization of atmospheric aerosols to understand the relationship between the chemical composition and physicochemical properties of organic aerosols and as a result their impact on the environment. In contrast to on-line techniques, these techniques are sample collection-based methods, employing solid deposition

substrates (such as membrane, glass or quartz fibre filters, or impaction plates) or a liquid (such as a wetted wall cyclone, impinger, or washing bottle), which should be stored, transported and prepared prior to the analysis.^{44,45} Despite the benefits of off-line techniques for identification and quantification of atmospheric aerosols, particularly through the coupling with pre-separation methods which can lead to unambiguous structure elucidation and quantification of aerosol compounds, they suffer from several drawbacks, sampling artefacts caused by evaporation of particle components, adsorption or absorption of additional gas phase components, and chemical reaction during sample collection, storage, transport, and preparation. Moreover, due to the requirements of the off-line techniques such as sample collection for several hours or days and sample storage and transportation, these techniques offer low temporal resolution.³⁴

On the other hand, the possibility of combining pre-separation techniques with a variety of different analytical techniques such as a Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR) and mass spectrometry (MS), makes off-line techniques powerful and robust tools to investigate atmospheric aerosols. However, despite the capability of FTIR and NMR for structural elucidation of unknown compounds, due to their distinct requirements, their application in atmospheric science remains limited. Over the past decades, off-line MS techniques have been exploited and developed significantly to study atmospheric aerosols. Nowadays, these techniques are used for molecular characterization of SOA, identification of source-specific markers and to study heterogeneous and condensed-phase reactions.¹³

2.3.2.1.2. Techniques based on mass spectrometry

The principle of MS techniques is to analyze compounds of interest (analytes) based on the ions they produce. These techniques involve three components: a ionization technique, a mass analyzer, and a detector. While detectors are fairly

common to all MS instruments, there are some ionization techniques that are suited to the analysis of organosulfates.

An ionization technique that has occasionally been employed for the analysis of organosulfates is electron ionization (EI) in combination with gas chromatography (GC) and prior conversion to trimethylsilyl derivatives that can be analyzed with GC/EI-MS. This approach allows the characterization of the non-sulfate part of the molecules.²⁷

By far the most employed MS ionization technique is electrospray ionization (ESI). This ionization technique is very suited to organosulfates because they can readily be deprotonated, resulting in deprotonated molecules that can be detected in the negative ion mode. ESI-MS can be applied directly to mixtures or in combination with a separation technique, mostly liquid chromatography (LC/MS). In the work performed within the frame of this thesis, only use was made of LC/ESI-MS. More details about this technique are provided in Chapter 3 (Section 3.6).

With regard to LC separation techniques, different techniques have been applied to organosulfates, including C₁₈ reversed-phase (RP) chromatography using a column that provides polar retention [e.g., the C₁₈ T3 column (Waters, Milford, MA, USA)], C₁₈ ion-pairing RP chromatography,⁴⁶ and hydrophilic interaction liquid chromatography (HILIC).^{2,47} More details about the first two techniques used in the present work are provided in Chapter 3 (Section 3.6.1.2).

Depending on the available instrumentation use can be made of tandem mass spectrometry and/or high resolution mass spectrometry.¹³ While high resolution MS allows to infer the molecular formula, tandem mass spectrometry (i.e., product ion scanning) allows to obtain information about the molecular mass, functional groups, and their location in the molecule. Information about the MS approaches used in the present work are provided in Chapter 3 (Section 3.6.2).

2.3.2.2. On-line techniques

2.3.2.2.1. Generalities

On-line techniques offer high time resolution which facilitate the understanding of highly dynamic systems with high temporal and spatial resolution that can be done in one step with no need for sample preparation. These techniques avoid potential artefacts associated with off-line analysis methods, such as evaporation and chemical reactions during long sample collection and analysis time periods.⁴⁸ Portable on-line mass spectrometers are usually small and have low power consumption with fast data acquisition rates and have been installed on numerous platforms, including ships, airplanes, and mobile trailers, to further understand the temporal and spatial variability of aerosol chemistry. However, when it comes to molecular and structural speciation, they fail to compete with off-line techniques.^{31,45}

On-line techniques are divided in two categories based on the targeted analysis: those that perform bulk measurements such as the Aerodyne aerosol mass spectrometer (AMS) and those that perform single particle measurements such as the aerosol time-of-flight (TOF) mass spectrometer.

2.3.2.2.2. On-line measurement of organosulfates

On-line MS techniques that have been applied with success to selected organosulfates (i.e., IEPOX sulfate) are particle aerosol laser MS and aerosol TOF-MS. Using the first technique IEPOX sulfate has been measured in airborne campaigns that were conducted in the southeastern USA and the tropics, and it was determined that IEPOX sulfate accounts for about 2-3% of the aerosol mass in the southeastern USA and higher fractions in the tropical free atmosphere.⁴⁹ IEPOX sulfate temporal profiles measured by aerosol TOF-MS in Atlanta (Georgia, USA) have also been reported.^{3,4}

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CHAPTER 3

Instrumentation and methods

3.1. Introduction

Off-line techniques based on a time-integrating sampling step (using filters, impactors, etc.) are used in the field and smog chamber experiments described in this thesis. A description of the instruments and methodology used for the collection and analysis of the samples, the smog chamber setup used for the production of SOA, and a description of the field site where ambient samples were collected, are given in this Chapter. General considerations about selection criteria are given as well. The general work flow for off-line aerosol analysis is shown in Figure 3.1 and can be divided in three steps: sample collection, sample preparation, and sample analysis.

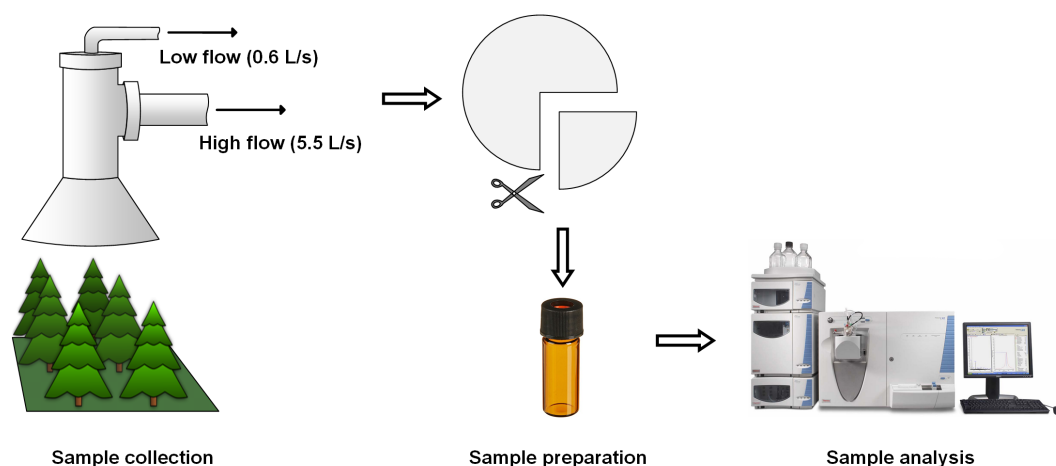


Figure 3.1. Work flow from sample collection until sample analysis.

3.2. Collection of ambient aerosols

Archived PM_{2.5} aerosol samples, collected from K-pusztá, Hungary, during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols) campaign between 22 May and 29 June 2006, were used. Day- and night-time samples were collected with a high-volume

dichotomous sampler (see Section 3.2.2) providing two size fractions, a fine (PM_{2.5}) and a coarse size fraction (with AD >2.5 µm). Pre-fired quartz fibre filters (Pall Corporation, Port Washington, NY, USA) were used as collection substrates for both the fine and coarse size fractions. Only the fine size fractions were used. The composition of atmospheric particulate matter during the BIOSOL campaign was studied and it was observed that the campaign time could be divided into two periods: from the start of the campaign until 11 June 2006 when it was unusually cold with daily maximum temperatures between 12 and 23 °C and from 12 June 2006 onward when the temperatures were considerably higher with daily maxima ranging from 24 to 36 °C.¹ The samples were archived in a freezer at – 25 °C.

3.2.1. Description of the field site, K-pusztá, Hungary

K-pusztá is a rural measurement site located on the Great Hungarian Plain (46°58'N, 19°35'E, 125 m above sea level), 15 km northwest from the nearest town Kecskemét, and 80 km southeast from Budapest. The K-pusztá site is and was used as one of the study sites within the European Monitoring and Evaluation Programme (EMEP), the European Supersites for Atmospheric Aerosol Research (EUSAAR), and the Aerosol, Clouds, and Trace gases Research InfraStructure Network (ACTRIS). It is and was the only Hungarian site within these programs. The surroundings of the measurement site are dominated by mixed forest (62% coniferous, 28% deciduous) and grassland (10%). The site is characterized by intense solar radiation during summer. The location of the site is shown in Figure 3.2 and indicated with a red asterisk.

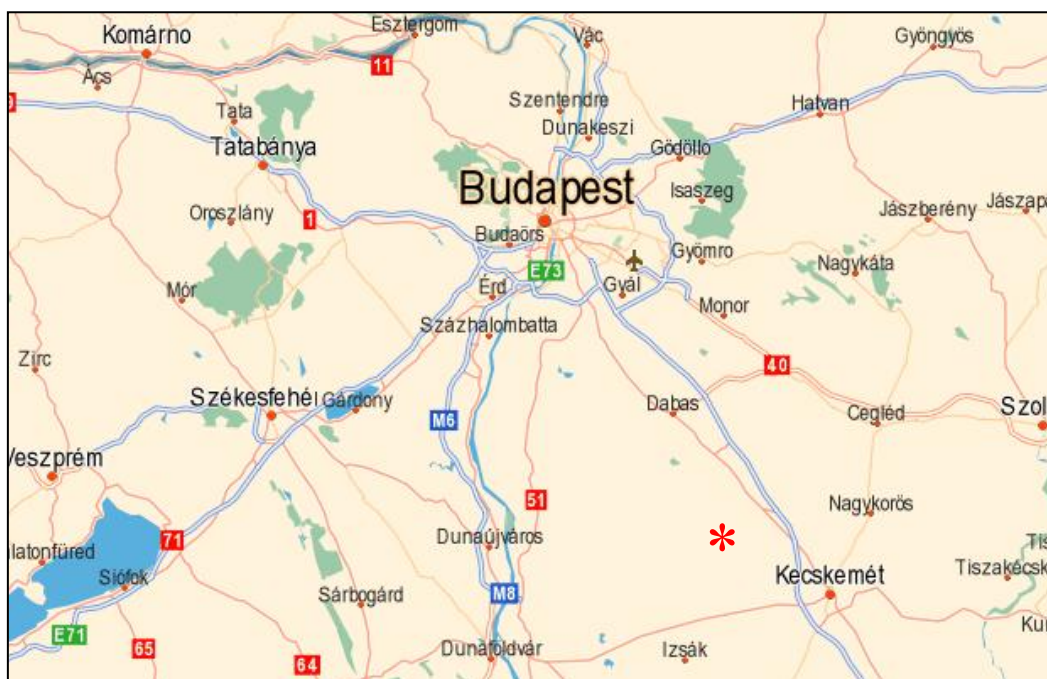


Figure 3.2. Location of the K-pusztasampling site, indicated with a red asterisk.

3.2.2. High-volume dichotomous virtual impactor

Aerosol particles were collected using a high-volume dichotomous virtual impactor (High-Vol). This collector was developed by Solomon et al. (1983).² The sampler uses a virtual impactor to separate the aerosol into two size fractions (coarse and fine) having an aerodynamic particle cutpoint of about $2.5 \mu\text{m AD}$. Figure 3.3 shows a cross section of the High-Vol. The impactor uses two 10-cm diameter filters supported in individual filter cassettes, leaving an effective sample collection diameter of just under 9 cm. Approximately 90% of the total air flow is removed perpendicular to the acceleration nozzle through the fine particulate filter and the remaining 10% passes through the coarse particulate filter. The air flow (suction) is produced by a high-volume pump that can operate at a total flow rate of up to 500 L min^{-1} .

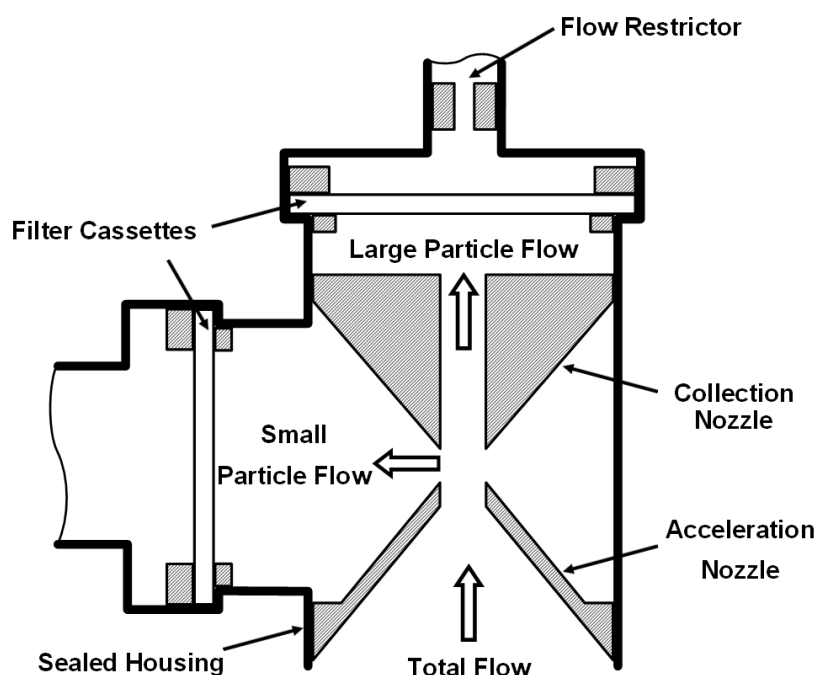


Figure 3.3. Cross section of a high-volume dichotomous virtual impactor. [adapted from Solomon et al., 1983]²

3.3. Smog chamber experiments

The experiments were conducted in a 14.5 m³ stainless-steel chamber with 40- μ m Teflon-coated walls.³ The temperature, aerosol size distribution, and relative humidity, as well as the O₃, nitric oxide (NO) and NO_x concentration were continuously measured. OH radicals were generated by photolysis of ozone in the absence of an OH scavenger. A mixture of sulfuric acid and ammonium sulfate (1/1; w/w) was used to create acidity in the chamber. The experiments were conducted in the dynamic mode (i.e., continuously stirred tank reactor). The reactants NO and the VOC precursor were continuously added from high-pressure cylinders to the reaction chamber through a mixing manifold. The steady-state nature of chamber operation allows for filter sampling for extended periods for

determining the composition of the resultant SOA. Once steady-state conditions were attained (24 h), samples for determining the composition of the SOA were collected on Teflon-impregnated glass fiber filters (Pallflex Fiberfilm, Pall Corporation, Port Washington, NY, USA).

Under the smog chamber conditions OH-initiated photooxidation takes place, giving rise to RO₂ radicals, which in the presence of NO and NO₂ will further react yielding RONO₂ and ROONO₂ species (Chapter 1; Fig. 1.3) as intermediate oxidation reaction products.

3.4. Sample preparation

In case of smog chamber SOA, the whole filter, and in case of ambient fine aerosol, sections of quartz fiber filters from different days and/or nights of the warm period of the campaign, were extracted 3 times for 30 min in an ultrasonic bath with 20 mL of methanol. The extracts were combined, concentrated in a rotary evaporator at 35 °C and 200 mbar to approximately 1 mL, filtered through a Teflon filter (0.45 µm), and evaporated to dryness under a nitrogen stream. The residue was redissolved in 1 mL of methanol and divided in five portions, which were dried under nitrogen, and the residues were stored at – 20 °C until use on different experimental days.

In case of analysis of smog chamber SOA, the residue was redissolved in 250 µL of methanol/water (1:1; v/v) before each series of LC/MS experiments by first dissolving the fraction in 125 µL of methanol and then adding 125 µL of water. In case of analysis of ambient fine aerosol, a portion containing 570 µg of organic carbon, as determined with a thermal-optical method,⁴ was redissolved before each series of LC/MS experiments in 1.5 mL of methanol/water (1:4; v/v) by first dissolving the fraction in 0.3 mL of methanol and then adding 1.2 mL of water. Afterwards, the sample was analyzed with LC/(–)ESI-MS using an aliquot of 5 µL. In the case of ion-pairing (IP) LC/MS, the IP reagent was placed in the

injection solution by adding 10 μL of 0.5 mol L^{-1} dibutylammonium acetate (DBAA) to 90 μL of the redissolved sample. Afterwards, the sample was analyzed with LC/(–)ESI-MS using an aliquot of 5 μL .

3.5. Sample analysis by liquid chromatography/mass spectrometry (LC/MS)

For analysis by LC/MS, an aliquot (typically 5 μL) of the reconstituted sample extract is injected onto an LC column. The sample is separated into its various components, which elute from the LC column and pass into the MS analyzer. The data from the MS analyzer are then stored and processed by the data system.

LC/MS is a powerful analytical technique that combines the separation capabilities of LC with the mass analysis capabilities of MS. This technique is used for the identification and quantification of chemicals in complex mixtures with very high sensitivity and specificity. Owing to substantial improvements during the last decade in the design of MS ion sources, more efficient ion trap designs, and more robust data systems, the coupling of high-performance LC (HPLC) instruments to MS instruments is not problematic anymore. A scheme of the LC/MS instrument (LXQ, Thermo Scientific, San Jose, CA, USA) used in this thesis work is presented in Figure 3.4.

A brief explanation of the main components of the LC/MS technique is given in the next sections.

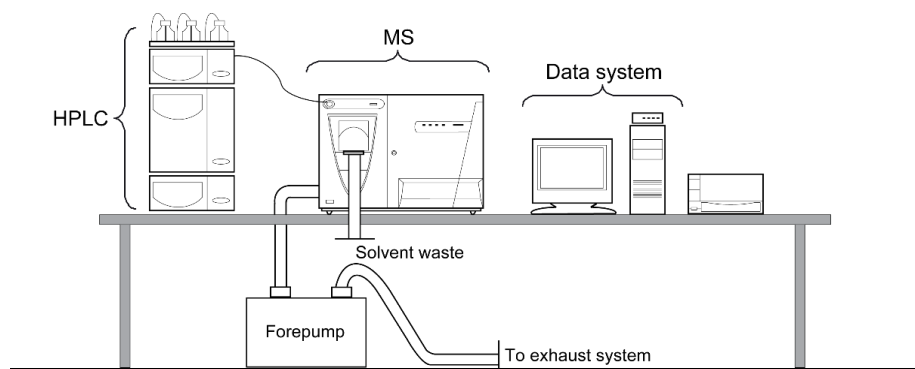


Figure 3.4. The main components of the LC/MS instrument used in this thesis work.

3.5.1. Liquid chromatography

The separation in LC is based on the interaction of the sample with the mobile and stationary phase, which leads to differential partitioning of the solutes between the mobile and stationary phase. Several different types of LC are available, which can be classified based on the physical state of employed stationary and/or mobile phases. The development of chemically bonded phases in the early 1970s had a major impact on the general practice of LC as modern synthetic techniques allowed for the tailoring of surface properties of inorganic oxides and porous polymers for specific applications across all separation modes. The Russian botanist Mikhail S. Tsvet discovered LC in 1903 by using columns of calcium carbonate for separating plant pigments, but operation at high pressures was not possible until the 1960s.⁵ Since then, the development of high-performance LC (HPLC) has been closely related with the introduction and development of column packing materials. An outstanding success was the development of hydrophobic surfaces for separations employing polar mobile phases (for most practical applications an aqueous solution) for reversed-phase (RP)-LC. RP-LC is now the most popular separation technique in LC, accounting for about two-thirds of all reported separations.⁵ Compared to the more traditional analysis by gas chromatography/ mass spectrometry (GC/MS) for which a derivatization step is needed, its use for separation of organic compounds in environmental and smog chamber samples has increased in the last decade.⁶⁻¹⁰ The experiments described in this thesis were performed using a Surveyor Plus HPLC system (pump and autosampler) (Thermo Scientific, San Jose, CA, USA).

3.5.1.1. The column

The key factor toward a successful analysis is the column selection.¹¹ Multiple stage oxidation of emitted biogenic and anthropogenic organic compounds in environmental conditions leads to the formation of polar compounds with lower

vapor pressure, which are present together with non-polar and inorganic salts in complex environmental samples.

In the present work, two different C₁₈ RP columns have been employed for the separation of the targeted organosulfate compounds, i.e., an Atlantis T3 column (3 µm; 2.1 x 150 mm) (Waters, Milford, MA, USA), which was used for regular RP-LC, and a C₁₈ Hypersil GOLD (Thermo Scientific, Waltham, MA, USA) (3 µm; 2.1 x 150 mm) column, which was employed for IP RP-LC. The C₁₈ Hypersil GOLD column contains a traditional fully-bonded and end-capped packing, whereas the Atlantis T3 column utilizes a trifunctional C₁₈ alkyl phase bonded at an intermediate ligand density (1.6 µmoles m⁻²) and is fully end-capped. Compared to a traditionally bonded and end-capped packing, the Atlantis T3 column RP sorbent shows improved retention, selectivity for polar analytes, superior column lifetime at low pH and better aqueous mobile phase compatibility.¹²

It is worth mentioning that HILIC using an ethylene bridged hybrid amide column has also very recently been used with success for the separation of organosulfates in ionic form.¹³

3.5.1.2. The mobile phase

The mobile phases for regular RP-LC consisted of 50 mM ammonium formate buffer pH 3 (A) and methanol (B). The applied 60-min gradient elution program was as follows: the concentration of eluent B was kept at 3% for 5 min, then increased to 95% in 15 min, kept at 95% for 25 min, then decreased to 3% in 10 min, and kept at 3% for 10 min. The samples were injected using a volume of 5 or 10 µL, and the flow rate was 0.2 mL min⁻¹.

The mobile phase gradient elution program applied in regular RP-LC is graphically shown in Figure 3.5 (bottom) together with the base peak chromatogram obtained for a regular RP-LC chromatographic run.

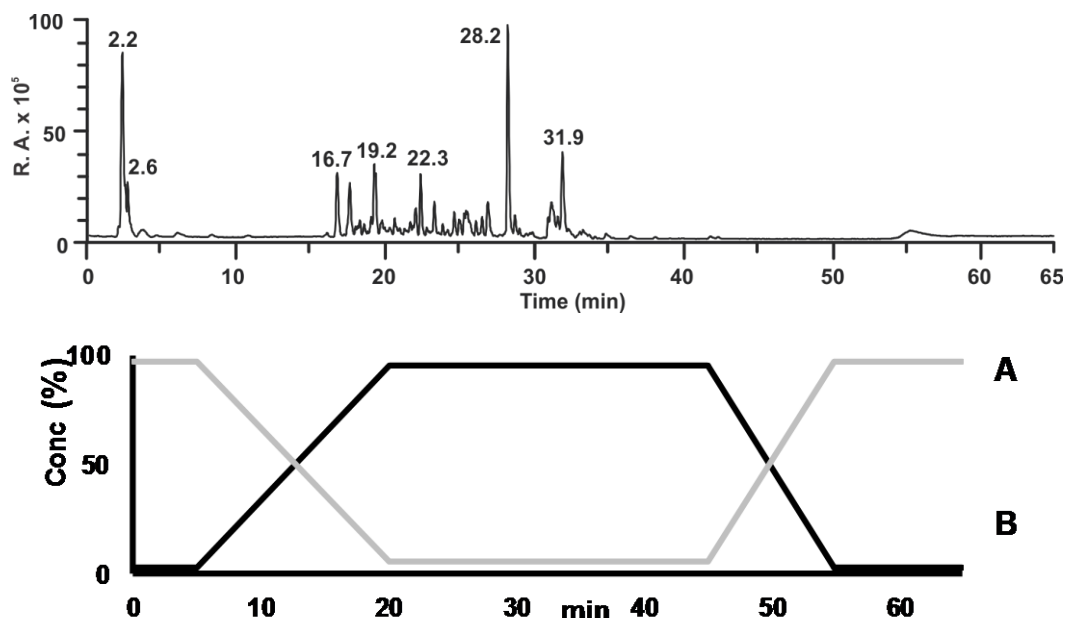


Figure 3.5. Top: base peak chromatogram (mass range m/z 50-500) for the regular RP-LC chromatographic run obtained for a methanol extract of $PM_{2.5}$ aerosol collected from K-pusztá, Hungary, during a 2006 summer period, and, bottom: gradient elution program applied.

The mobile phases for ion-pairing RP-LC consisted of 50 mM DBAA in water (A), acetonitrile (B), and water (C). The applied 70 min gradient elution program was as follows: the concentration of eluent A was kept at 10% during the whole 70 min program; the concentration of water (C) was kept at 3% for 10 min, then increased to 87% in 15 min, kept at 87% for 25 min, then decreased to 3% in 10 min, and kept at 3% for 10 min. The injection volume and flow rate were 5 μ L and 0.2 mL min^{-1} .

3.5.2. Mass spectrometry: background and operation principles

Mass spectrometry is an analytical chemistry technique which is widely used to identify unknown compounds, elucidate the structure and chemical properties of

molecules, and quantify compounds by measuring the mass-to-charge (m/z) ratio and abundance of gas-phase ions.^{14,15}

A mass spectrometer consists of three components: an ion source, a mass analyzer, and a detector (Figure 3.6). (1) The ionizer (the source) converts a portion of the sample provided through an inlet into gaseous ions; (2) the mass analyzer sorts the gas-phase ions by their m/z values; and (3) the detector measures the value of an indicator quantity and provides output signals proportionally to the relative abundance of each ionic species present. Each of these elements exists in many forms and is combined to produce a wide variety of MS instruments with specific characteristics.

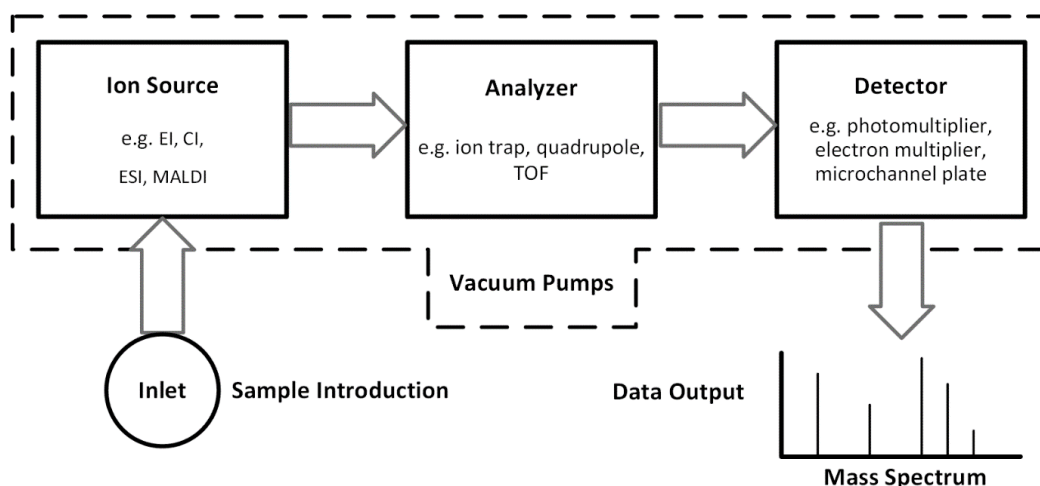


Figure 3.6. Schematic of a typical mass spectrometer. Abbreviations: CI, chemical ionization; MALDI, matrix-assisted laser desorption ionization.

The mass spectrometer used in this thesis work was an LXQ instrument (Thermo Scientific, San Jose, CA, USA). This instrument basically consists of an atmospheric pressure ionization (API) source, ion optics, a mass analyzer (i.e., a linear ion trap), and an ion detection system. In addition, occasional use was also

made of high-resolution instruments for accurate mass measurements of precursor as well as MS² product ions. The instruments used for this purpose were: (1) an LTQ-Orbitrap mass spectrometer ((Thermo Scientific) (Chapters 4 and 6), based on an Orbitrap analyzer,¹⁶ and a Synapt G2-S HDMS mass spectrometer (Waters) (Chapter 7), based on a reflectron time-of-flight analyzer.¹⁶

Ionization of the sample takes place in the API source. The specific method used to ionize the sample is referred to as the ionization technique (see Section 3.6.2.1). The ions produced in the API source are transmitted by the ion optics into the mass analyzer, where they are trapped in stable orbits by a time-varying electric field. The polarity of the potentials applied to the API source and ion optics determine whether positively charged ions or negatively charged ions are transmitted to the mass analyzer. The m/z ratios of the ions produced in the API source are measured by the mass analyzer. Selected ions are ejected from the mass analyzer and reach the ion detection system where they produce a signal which is then amplified by the detection system electronics.

3.5.2.1. Electrospray ionization

Electrospray ionization (ESI) was discovered in 1984 by Yamashita and Fenn.^{17,18} ESI is referred to as a soft ionization technique because it ionizes the sample molecules in solution into ions in the gas phase without extensive fragmentation. Therefore, this technique is suitable to analyze any polar compound that makes an ion or adduct ion in solution and is especially useful for the mass analysis of polar compounds. The targeted organosulfate analytes are well suited for ESI since they contain a sulfate group which can readily be deprotonated, giving rise to deprotonated molecules ($[M - H]^-$) which are detected in the negative ion mode. In the ESI technique, ions are produced and analyzed as follows:

- 1) A high voltage (3-6 kV) is applied to the sample solution in the ESI needle, which causes ions of the same polarity to leave the solution surface and form a “Taylor cone”.
- 2) Electrically charged fine droplets are sprayed through the ESI needle. Fine charged droplets are electrically charged with ions of both polarities but with an excess of ions with the same polarity as the applied voltage.
- 3) Due to the solvent evaporation, the electrical charge density at the surface of the droplets increases.
- 4) When the electrical charge density at the surface of the droplets reaches a critical point, known as the Rayleigh stability limit, the electrostatic repulsion becomes greater than the surface tension and the tiny charged droplets are cleaved into smaller droplets.
- 5) From the very small, highly charged droplets, sample ions are ejected into the gas phase. This mechanism, also called “ion evaporation”, has been suggested by Iribane and Thomson.¹⁹
- 6) The sample ions pass through an ion transfer capillary, enter the mass analyzer and are analyzed.

The ESI process is presented in Figure 3.7.

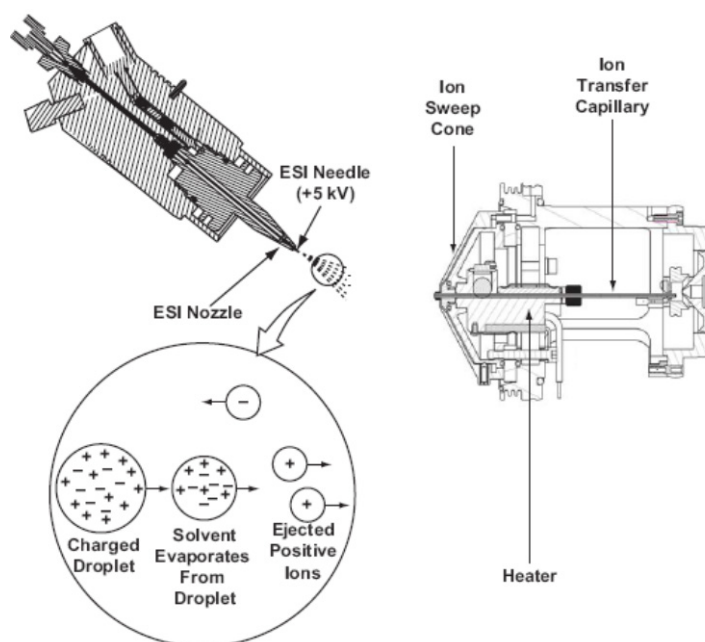


Figure 3.7. The ESI process (positive ion mode).

There are two major theories that explain the final production of gas-phase ions: the ion evaporation model and the charge residue model. The ion evaporation model, proposed by Iribane and Thomson,¹⁹ suggests that as the droplet reaches a certain radius the field strength at the surface of the droplet becomes large enough to assist the field desorption of solvated ions. This theory was further refined by Vertes and co-workers, who provided evidence for a solvated ion evaporation process.²⁰ The charge residue model was proposed by Dole and co-workers²¹ and suggests that electrospray droplets undergo evaporation and fission cycles, eventually they reach the Raleigh limit leading to progeny droplets that contain on average one analyte ion or less. The gas-phase ions form after the remaining solvent molecules evaporate, leaving the analyte with the charges that the droplet carried.

3.5.2.2. Ion optics

The ions produced in the API source are focused and transmitted into the trap by the ion optics. The ions keep moving in the direction of lower potential energy (net decreasing voltages) towards the mass analyzer.

In the LXQ mass analyzer, the ion optics consists of a radio frequency (RF) lens and two ion guides (Q00/L0 RF lens, Q0 quadrupole and Q1 octapole). These components are shown in Figure 3.8.

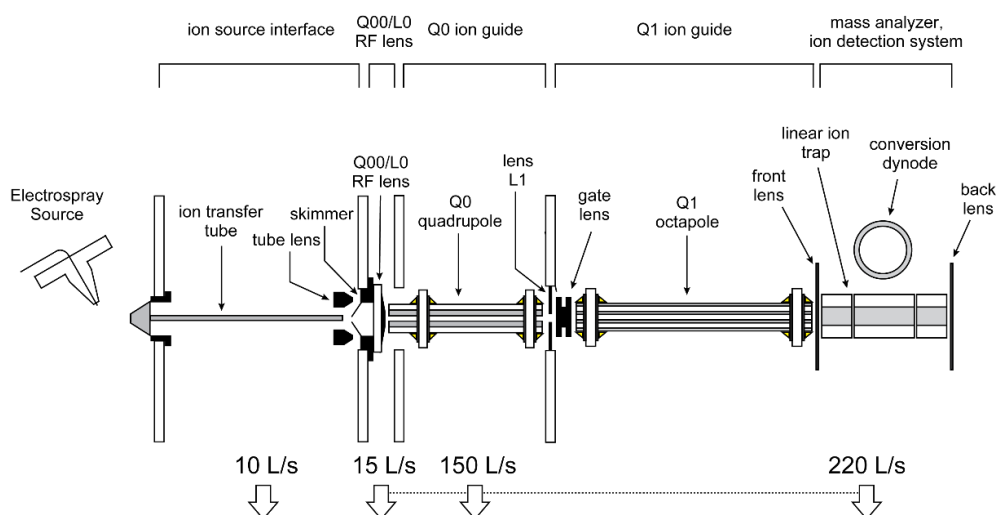


Figure 3.8. The overall configuration of the LXQ instrument.

The Q00 RF lens is a square array of square-profile segments which acts as an ion focusing device. An RF voltage applied to the optics gives rise to an electric field that focuses the ions along the axis of the Q00 RF lens. A direct current (DC) voltage offset from ground applied to the Q00 RF lens - called the Q00 offset voltage - increases the translational kinetic energy of ions emerging from the skimmer.

The lenses L0 and L1 act as ion focusing devices; they are metal disks with a circular hole in the center through which the ion beam can pass. An electrical potential can be applied to the lenses to accelerate (or decelerate) ions as they approach the lens and to focus the ion beam as it passes through the lens. These lenses also act as a vacuum baffle between the different ion optic chambers.

The Q0 quadrupole is a square array of square-profile rods which acts as an ion transmission device. An RF voltage applied to the rods gives rise to an electric field that guides the ions along the axis of the quadrupole. The Q1 octopole works in the same way, the difference is that this multipole has round-profile rods.

The gate lens is used to start and stop the injection of ions into the mass analyzer.

3.5.2.3. Analyzer

The mass analyzer is the site of mass analysis (that is, ion storage, ion isolation, collision-induced dissociation, and ion scan out). The mass analyzer in the LXQ instrument consists of a front lens, a linear ion trap, and a back lens (Figure 3.8). The front and back lenses are metal disks with a circular hole in their center through which the ion beam can pass. The purpose of the front and back lenses is to provide conductance limits. During ion injection the back lens is +12 V relative to the trap and the front lens potential relative to the trap is adjustable by the user. During scan out both lenses are +200 V relative to the trap for positive ions and – 200 V relative to the trap for negative ions.

The linear ion trap is a square array of precision-machined and precision-aligned hyperbolic rods. Two of these rods have a slot in the center section through which the ions are ejected during scan out. Ions leaving only one of the slots are detected in this instrument. Quartz spacers act as electrical insulators between adjacent rods. Rods opposite to each other in the array are connected electrically.

The linear ion trap, also known as two-dimensional (2-D) quadrupole, has better trapping efficiency and increased ion capacity relative to a three-dimensional (3-D) ion trap.²²

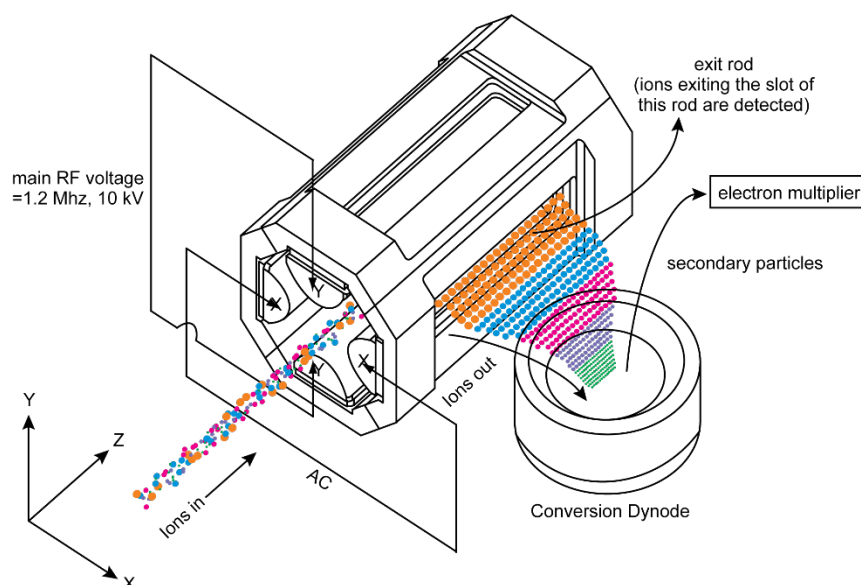


Figure 3.9. The LXQ linear ion trap quadrupole rod assembly.

The operation of the linear ion trap requires three sets of voltages:

- 1) DC voltages applied to each component of the mass analyzer, which establish axial trapping by lowering the ion trap potential below the front and back lenses (Figure 3.8). These DC axial trapping voltages allow the mass analyzer to perform its storage and scan out functions.
- 2) The main RF voltage. The RF voltage is applied only to the y rods and is of constant frequency (1.2 MHz) and of variable amplitude (0 to 10,000 V zero-to-peak). The application of the main RF voltage to the y rods produces a two-dimensional quadrupole field within the mass analyzer cavity. This time-varying field drives ionic motion in the radial (X,Y) directions. When the amplitude of the main RF voltage is low, all ions above a minimum m/z ratio

are trapped (storage voltage). As the main RF voltage increases, ions of increasing m/z ratio become successively unstable in the X direction and are ejected from the mass analyzer. Many of these ions are detected by the ion detection system.

- 3) The ion isolation waveform voltage, resonance excitation alternate current (AC) voltage, and resonance ejection AC voltage. These voltages are applied to the x rods (Figure 3.9) to stimulate motion of the ions in the direction of the ion detection system. The voltages applied to the x rods are equal in amplitude but are 180° out of phase to one another. When the AC frequency applied to the x rods equals the resonance frequency of a trapped ion, which depends on its mass, the ion gains kinetic energy. If the magnitude of the applied voltage is sufficiently large or the ion is given sufficient time, the ion is ejected from the mass analyzer in the direction of the ion detection system (through the slot in one of the x rods as shown in Figure 3.9).

The ion isolation waveform voltage consists of a distribution of frequencies between 5 and 600 kHz containing all resonance frequencies except those corresponding to the ions to be trapped. The ion isolation waveform voltage acts during the ion isolation step of selected ion monitoring (SIM), selected reaction monitoring (SRM) or MS^n ($n > 1$) full scan applications. The ion isolation waveform voltage, in combination with the main RF voltage, ejects all ions except those of a selected m/z ratio or narrow ranges of m/z ratios.

The resonance excitation AC voltage is applied to the exit rods to fragment precursor ions into product ions during the collision-induced dissociation step of SRM or MS^n ($n > 1$) full scan applications. The resonance excitation AC voltage is not sufficiently strong to eject an ion from the mass analyzer. However, ion motion in the radial direction is enhanced and the ion gains kinetic energy. After many collisions with the helium damping gas, which is present in the mass

analyzer, the ion gains sufficient internal energy to cause it to dissociate into product ions. The product ions are then mass-analyzed.

The resonance ejection AC voltage is applied during ion scan out. The resonance ejection AC voltage is applied at a fixed frequency and increasing amplitude during the ramp of the main RF voltage. As a result, the ejection of the ion is facilitated, and mass resolution is significantly improved.

3.5.2.4. Analyzer operation

There are four basic steps to all ion trap operations: trapping, isolation, excitation, and ejection. Any scan event that is completed in the LXQ instrument does so by applying some order of these steps.

In all scan events, the first step is collection, in which all ions, regardless of their m/z value, are allowed to enter the ion trap and are retained. In step 2 a series of processes can be completed on the ions before they are eventually ejected (step 3) from the trap to the ion detection system in a controlled fashion such that the m/z value can be monitored. In the simplest case of a full scan, all of the ions are collected and then ejected, resulting in a spectrum that displays the ion count of each m/z value initially entering the trap. In the case of SIM, the ions are collected as before, but during the time in which the ions are maintained in the trap, voltages are altered to isolate a single ion or ion window, thus retaining only the ion of interest and purging everything else. When the ejection step is completed this time, the only ion scanned out is the ion specified. In the case of MS/MS, the ions are collected and a single precursor ion is isolated as in the case of SIM. Then, voltages are applied to excite and fragment that precursor ion into product ions all of which can then be scanned out. For any higher level of analysis, such as SRM or MS^n , steps 2 and 3 are repeated to yield the desired end-product ions, which are eventually scanned out in step 4. For example, in order to perform an MS^3 full scan, the step order would be to collect everything (step 1), isolate a

single precursor ion (step 2), excite that ion to fragment it into several product ions (step 3), isolate one of those product ions (step 2 again), excite that single isolated product ion (step 3 again), and then eject all of the second-generation product ions (step 4).

3.5.3. Operating conditions for the LXQ instrument

For most of the LC/(-)ESI-MS analyses a linear ion-trap mass spectrometer (LXQ, Thermo Scientific) was operated under the following conditions: sheath gas flow (nitrogen), 50 arbitrary units; auxiliary gas flow (nitrogen), 5 arbitrary units; source voltage, - 4.5 kV; capillary temperature, 350 °C; and maximum ion injection time, 200 ms. For MS², MS³ and MS⁴ experiments, an isolation width of 2 *m/z* units and a normalized collision energy of 35% were applied. The [M - H]⁻ signal optimization was done by introducing a 50 µg mL⁻¹ *cis*-pinonic acid standard solution. The MS system employed in this thesis work uses Xcalibur version 2.0 software (Thermo Scientific).

3.6. References

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CHAPTER 4

Mass spectrometric characterization of organosulfates related to secondary organic aerosol from isoprene

Adapted from:

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4.1. Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant nonmethane hydrocarbon emitted into the Earth's atmosphere, mainly by deciduous trees, with emissions estimated at 410 Tg C yr^{-1} on average.¹ The formation of low-volatility compounds during isoprene oxidation has been estimated to be the single largest source of SOA.²⁻⁵ Organosulfates are low-volatility compounds that result from the particle-phase sulfation of epoxy- and hydroxyl-containing SOA compounds with ammonium bisulfate aerosol.⁶⁻¹¹ The latter aerosol is formed under ambient conditions from the neutralization of sulfuric acid, which in turn is generated by the oxidation of sulfur dioxide and is thus mainly of anthropogenic origin in continental regions of the globe.¹² Analysis of laboratory-generated SOA and fine ambient aerosols by LC coupled with ESI-MS in the negative ion mode has provided evidence for the presence of numerous organosulfates which can be related to SOA from isoprene, unsaturated fatty acids, and monoterpenes.⁶⁻¹¹ Some of the most polar organosulfates are related to SOA from the photooxidation of isoprene because of the presence of several additional polar groups such as hydroxyl and carboxyl groups. Of the isoprene SOA-related organosulfates, the most abundant compounds present in ambient fine aerosol from different forested sites have been firmly established as 2-methyltetrol organosulfates,^{6,9-11} which are formed by sulfation of C_5 -epoxydiols, second-order photooxidation products of isoprene.^{11,13} A second abundant isoprene SOA-related organosulfate has been identified as 3-sulfooxy-2-hydroxy-2-methylpropanoic acid, a sulfate ester of 2-methylglyceric acid.^{6,10} The latter acid can be regarded as a further reaction product of methacrolein, which is a major gas-phase oxidation product of isoprene.^{14,15} In addition, a number of organosulfates containing one or two nitrooxy groups have been found to be

related to isoprene SOA and have been identified as 2-methyltetrol-related nitrooxy organosulfates.^{6,8,9}

The present study is an extension of earlier work of our laboratory on the characterization of polar organosulfates that occur in fine ambient aerosols from forested sites^{9,10} and are of climatic relevance because of their capacity to increase the hydrophilic properties and thus the cloud condensation nuclei effects of the aerosol. Here, we focus on the characterization of additional isoprene SOA-related organosulfates, which have not been covered in earlier work or require a revision of their structures. The mass spectral data obtained for selected unknown polar organosulfates present in ambient fine aerosols, collected from K-pusztá, Hungary, during a warm summer period, have been interpreted in detail and tentative structures for them are proposed. The K-pusztá site was selected because isoprene SOA formation is known to be significant during summer.^{16,17} The structures were investigated by LC/(–)ESI-MS and conversion of carbonyl-containing OSs into 2,4-dinitrophenylhydrazone derivatives. The use of (–)ESI is suitable for the sensitive detection of organosulfates, because the sulfate group is readily deprotonated during the ionization process, whereas the combination with linear ion trap mass spectrometry¹⁸ allows one to obtain good-quality MS² and MS³ product ion spectra during the elution of a chromatographic peak.

On the other hand, derivatization of carbonyl-containing OSs to 2,4-dinitrophenylhydrazones allows one to confirm the presence of a carbonyl group in the molecules. Derivatization of carbonyl compounds to 2,4-dinitrophenylhydrazones has been employed for LC/MS analysis because these derivatives are suitable for detection in (–)ESI.¹⁹⁻²¹ As in previous work dealing with the characterization of organosulfates from the oxidation of isoprene, unsaturated fatty acids, and/or monoterpenes,^{9,10,22} we apply in the present study LC/(–)ESI-linear ion trap MS methodology and detailed interpretation of the mass spectral data to structurally

characterize polar OSs. Caution is, however, required with regard to the structural elucidation of unknown compounds using the latter approach since the assignments remain tentative. Therefore, in an effort to unambiguously characterize an abundant organosulfate (MW 184) present in an ambient fine aerosol, we have also synthesized two candidate molecules and have compared their LC/MS properties with those of the unknown compound.

4.2. Experimental section

4.2.1. Chemicals

Methanol (ULC/MS grade), used for sample preparation and as the LC mobile phase, and acetonitrile (HPLC supragradient grade), used for DNPH-reagent preparation, were from Biosolve NV (Valkenswaard, The Netherlands); ammonium formate (analytical grade) and *cis*-pinonic acid (purity: 98%) were from Sigma-Aldrich (St. Louis, MO, USA); acetic acid (analytical grade) was from Merck (Darmstadt, Germany). 2,4-Dinitrophenylhydrazine (DNPH) was obtained from Sigma-Aldrich (purity $\geq 99\%$, delivered in 50% water) and the moisture was removed prior to use by a double recrystallization from acetonitrile. The thus obtained DNPH crystals were used for the preparation of an acidified derivatization solution that contained 10 mM DNPH and 1.5 M acetic acid in acetonitrile. High-purity water (18.2 M Ω ·cm; total organic carbon: 2 ppb), used for redissolving aerosol extracts and preparing the aqueous LC mobile phase, was supplied by a Milli-Q water purification system (Millipore, Bedford, MA, USA). The following chemicals were used for the organic synthesis of reference organosulfates: crotonaldehyde (predominantly *trans*) and *m*-chloroperoxybenzoic acid (77%) (Sigma-Aldrich); ethylene glycol (Fluka, Buchs, Switzerland); oxalic acid and magnesium sulfate (anhydrous) (Merck); benzene (TCI, Europe N.V. Zwijndrecht, Belgium); and potassium carbonate (anhydrous), potassium

hydroxide (85%), and *p*-toluenesulfonic acid (monohydrate) (Acros Organics, Geel, Belgium).

4.2.2. Organic synthesis of reference organosulfates

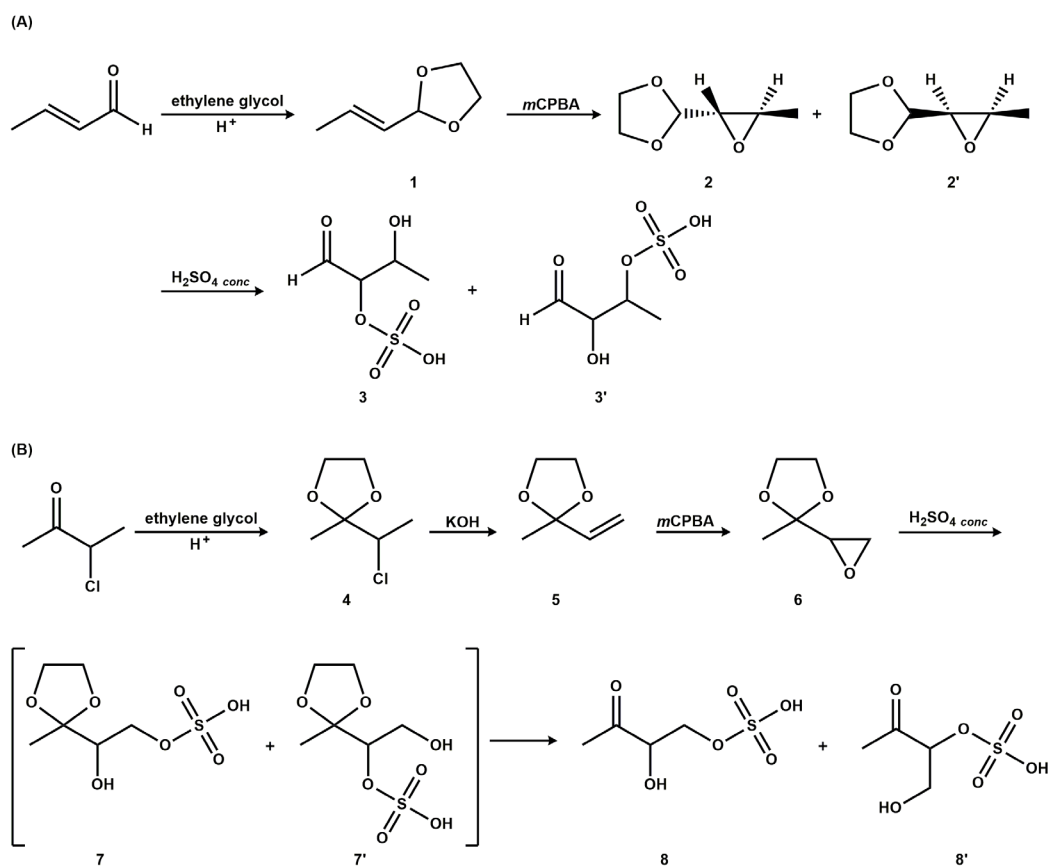
The synthetic procedure leading to the organosulfates of 2,3-dihydroxybutanal (**3** and **3'**) and 3,4-dihydroxy-2-butanone (**8** and **8'**) are given in Scheme 4.1, and are briefly summarized below.

4.2.3. Organosulfates of 2,3-dihydroxybutanal (**3** and **3'**)

To obtain epoxide **2**, crotonaldehyde was first converted into acetal **1**, which was then reacted with ethylene glycol in the presence of anhydrous MgSO₄ and catalyzed by oxalic acid instead of *p*-toluenesulfonic acid in order to avoid a side reaction (addition of ethylene glycol to the double bond).²³ The latter was then epoxidized with *m*-chloroperoxybenzoic acid (*m*CPBA).^{24,25} Further reaction of epoxide **2** with concentrated sulfuric acid in acetone resulted in the formation of a mixture of organosulfates **3** and **3'**.²⁶

4.2.4. Organosulfates of 3,4-dihydroxy-2-butanone (**8** and **8'**)

Epoxide **6** was synthesized according to literature procedures.^{24,27} First, 3-chlorobutan-2-one was converted into its acetal **4** in a standard reaction with ethylene glycol catalyzed by *p*-toluenesulfonic acid. An alkali-induced abstraction of hydrogen chloride from **4** generated a double bond and gave rise to alkene **5**, which was further epoxidized with *m*CPBA.^{25,27} Subsequently, epoxide **6** was reacted with concentrated sulfuric acid in acetone,²⁶ leading to ring opening and deprotection, and resulting in the formation of a mixture of organosulfates **8** and **8'**.



Scheme 4.1. Synthetic procedures leading to the organosulfates of (A) 2,3-dihydroxybutanal (**3** and **3'**) and (B) 3,4-dihydroxy-2-butanone (**8** and **8'**).

4.2.5. Aerosol samples and sample preparation

See Chapter 3, Sections 3.2 and 3.4.

In case of derivatization, DNPH-derivatives were prepared by adding 25 mL of the derivatization mixture to 250 mL of the filter extract. The mixture was left at room temperature overnight to enable complete derivatization of compounds containing (a) carbonyl group(s). Afterwards, the sample was analyzed using LC/(–)ESI-MS.

4.2.6. Liquid chromatography

Use was made of regular RP-LC with an Atlantis T3 column. See Chapter 3, Section 3.5.1 for further details.

Compared with earlier work,¹⁰ improved chromatographic peak shapes of the early-eluting polar organosulfates were obtained by using a 50 mM ammonium formate buffer pH 3 instead of 0.1% aqueous acetic acid as the mobile phase. The injection volume and flow rate were 10 mL and 0.2 mL min⁻¹, respectively.

4.2.7. Mass spectrometry

A linear ion trap mass spectrometer (LXQ, Thermo Scientific) was used in this work; for the operation conditions, see Chapter 3, Section 3.6.3.

Accurate mass measurements were carried out using an LTQ Orbitrap XL mass spectrometer (Thermo Scientific) equipped with an Accela LC system (Thermo Scientific). The LTQ Orbitrap XL mass spectrometer was equipped with an ESI source operating in the negative ion mode under the same conditions as described above for the ion trap experiments on the LXQ instrument. Accurate mass measurements were only carried out for the ambient K-pusztá PM_{2.5} aerosol extract in the MS² mode, and were mainly performed to obtain accurate mass data on the deprotonated molecules and to differentiate between ambiguous neutral mass losses [e.g., 44 (CO₂ or C₂H₄O), 30 (CH₂O or C₂H₆)] from the precursor ions. The mass resolution was set at 30,000 and the source parameters were tuned for maximum sensitivity. An isolation width of 2 *m/z* units and a normalized collision energy level of 35% were applied. Data were acquired and processed using Xcalibur 2.07 software. The mass accuracy was better than 1 mDa.

4.3. Results and discussion

Figure 4.1 shows selected LC/MS data obtained for the K-pusztá fine aerosol, including a base peak chromatogram (BPC) and extracted ion chromatograms (EICs) at *m/z* 215, 199, 183, 169 and 155, corresponding to OSs that are related to

isoprene SOA. Some of the targeted OSs are known, have already been partly characterized in previous studies,¹⁰ and/or need a revision of their structures. The most abundant polar OSs are the m/z 215 compounds [retention time (RT) 2.58 min], known to correspond to isomeric 2-methyltetrol OSs formed in the particle phase by reaction of isoprene derived C₅-epoxydiols with sulfuric acid or ammonium sulfate seed aerosols.^{11,13} It should be noted, however, that these compounds have not been fully characterized and that the location of the sulfate groups has not yet been firmly established. It can be seen from the EIC data that the other targeted OSs at m/z 199, 183, 169 and 155 are also rather abundant, with an abundance for the major ones at each m/z value higher than 10% of that of the m/z 215 compounds. As will be outlined in the section below, the m/z 169 and 155 compounds were wrongly assigned in a previous study¹⁰ and their structures have, therefore, been addressed here. Conversely, the structure of an unknown m/z 199 OS, which is related to the m/z 155 organosulfate, also requires revision.

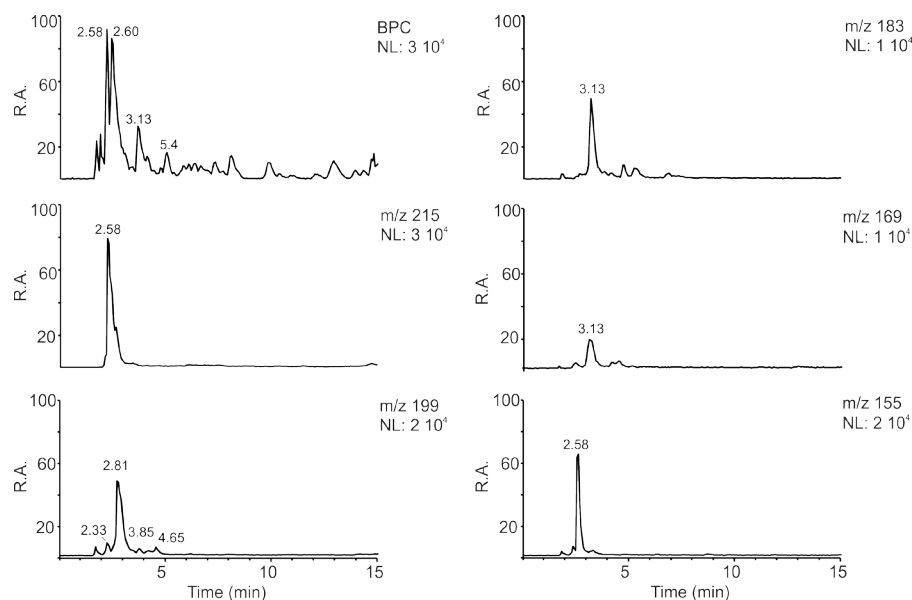


Figure 4.1. Selected LC/MS chromatographic data [base peak chromatogram (BPC) and extracted ion chromatograms (EICs)] obtained for K-pusztá PM_{2.5} aerosol. NL: normalization level.

4.3.1. MW 156 and 170 organosulfates

The isoprene SOA-related m/z 155 (RT: 2.58 min; $C_2H_3O_6S$; measured mass: 154.98152; error: 0.54 mDa) and 169 OSs (RT: 3.13 min; $C_3H_5O_6S$; measured mass: 168.98152; error: 0.2 mDa) have been assigned in previous work to sulfuric acid adducts of glyoxal and methylglyoxal.¹⁰ However, their structures have recently been revised as the organosulfate esters of glycolic and lactic acid, and these assignments have been supported through the synthesis of authentic standards.²⁸ It has been shown that the sulfate ester of glycolic acid sulfate is formed upon the reactive uptake of glyoxal on ammonium sulfate seed aerosol under irradiated conditions although the underlying photochemistry is not clear;²⁹ a similar mechanism may operate in the formation of lactic acid sulfate from methylglyoxal. Globally, the majority of glyoxal (47%) and methylglyoxal (79%) comes from isoprene.³⁰ However, considering that glyoxal and methylglyoxal have sources other than isoprene, such as, for example, aromatics (e.g., toluene and *m*-/*p*-xylene),³¹ the sulfate esters of glycolic and lactic acid cannot be considered as specific isoprene SOA tracers. The m/z 155 and 169 MS^2 product ion spectra are presented in Figures 4.2(A) and 4.2(B). These spectra are dominated by the bisulfate anion (m/z 97), whereas the product ion at m/z 111 or 125, corresponding to the loss of CO_2 (44 u) and characteristic for a carboxyl group, is rather weak. The presence of a sulfate group at the 2-position of glycolic and lactic acid organosulfates preferentially gives rise to the formation of the bisulfate anion (m/z 97), probably due to a favorable interaction between the sulfate group and the neighboring carboxyl group, thus competing with the loss of CO_2 from the carboxyl group (Scheme 4.2).

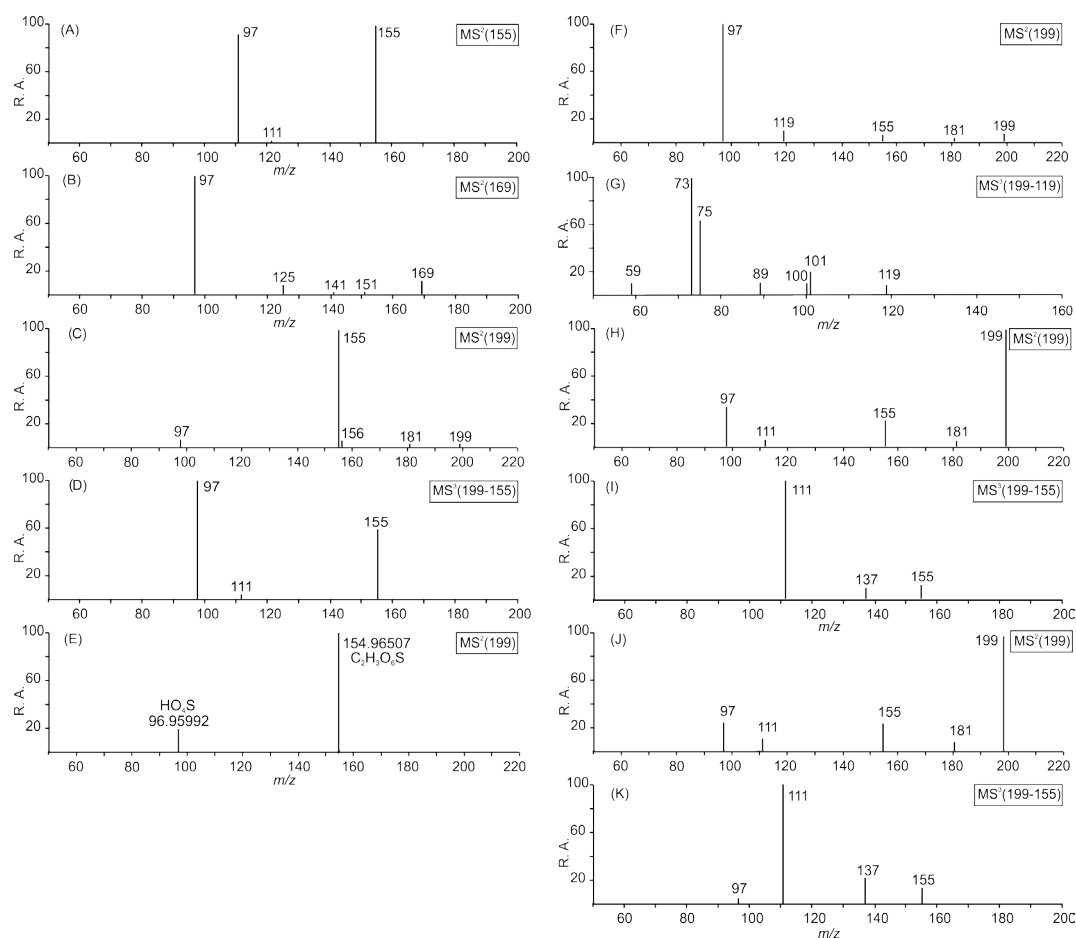
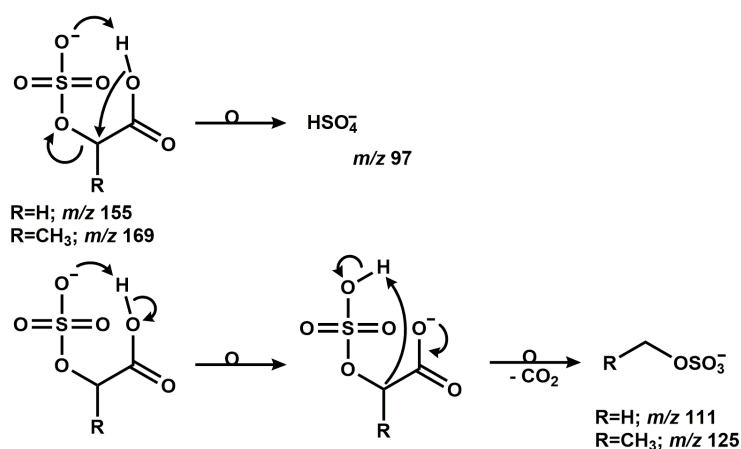


Figure 4.2. Selected LC/MS data (MS^2 and MS^3 product ion spectra) obtained for compounds with a MW of (A) 156, identified as glycolic acid organosulfate (OS) [retention time (RT), 2.58 min; Fig. 1]; (B) 170, identified as lactic acid OS (RT 3.13 min); (C–E) 200, identified as glycolic glycolate OS (RT 2.33 min); (F, G) 200, identified as 2-methylglyceric acid OS (RT 2.81 min); and (H–K) 200, identified as 2,3-dihydroxybutanoic acid OSs (RTs, 3.85 and 4.65 min). All MS data were obtained with the LXQ instrument, except the data shown in (E) which were obtained with the LTQ Orbitrap XL instrument.

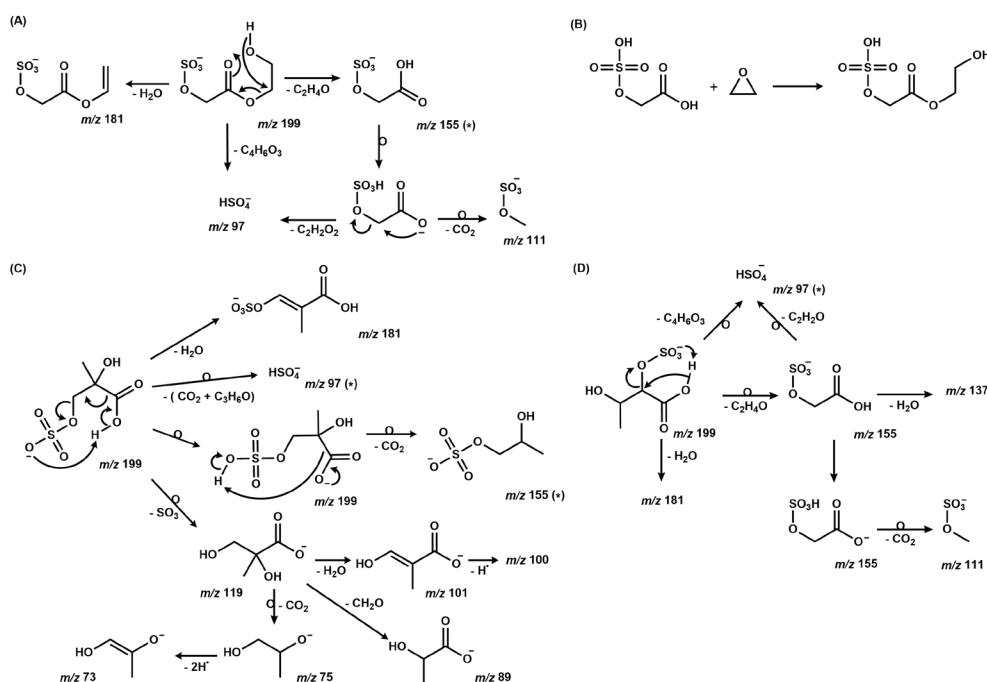


Scheme 4.2. Proposed fragmentation pathways for deprotonated glycolic (*m/z* 155) and lactic acid organosulfates (*m/z* 169).

4.3.2. MW 200 organosulfates

Several peaks can be observed in the *m/z* 199 EIC (Fig. 3.1); we will first address the *m/z* 199 OS (C₄H₇O₇S; measured mass: 198.99231; error: – 0.1 mDa) eluting at 2.33 min, which is related to the *m/z* 155 compound which is assigned to glycolic acid OS. Selected MS data are shown in Figures 4.2(C) and 4.2(E), and Scheme 4.3(A). The *m/z* 199 MS² spectrum is dominated by *m/z* 155, while the *m/z* 199 → *m/z* 155 MS³ spectrum is similar to the *m/z* 155 MS² spectrum obtained for deprotonated glycolic acid OS [Fig. 4.2(A)]. On this basis, it can be concluded that the *m/z* 199 compound is a derivative of glycolic acid OS, where the additional part has a mass of 44 units (u). This mass corresponds to C₂H₄O, as supported by accurate mass measurement of *m/z* 155 [C₂H₃O₆S; measured mass: 154.96507; error: 0.6 mDa; Fig. 4.2(E)]. It is noted that the loss of C₂H₄O does not involve participation of the charge, a reaction that bears similarity to charge-remote fragmentation occurring in even-electron precursor ions containing one or more double bonds.³² Taking into account possible reactions that might occur in the atmosphere, this unknown compound is tentatively attributed to a glycol ester of glycolic acid OS. This compound could be formed by reaction of glycolic acid

OS with oxirane [Scheme 4.3(B)], a compound which has both natural and anthropogenic sources.³³ An alternative source for oxirane could be the reactive uptake and subsequent catalytic oxidation, in the particle phase,³⁴ of ethene, a volatile with a significant biogenic source.³⁵



Scheme 4.3. Proposed (A) fragmentation and (B) formation pathway for the unknown MW 200 compound, attributed to glycolic glycolate organosulfate; proposed fragmentation pathways for (C) the isoprene SOA-related 3-sulfooxy-2-hydroxy-2-methylpropanoic acid and (D) the unknown minor crotonaldehyde SOA-related MW 200 organosulfates. The pathways outlined with arrows correspond to the ions indicated with an asterisk (*).

The major m/z 199 compound ($\text{C}_4\text{H}_7\text{O}_7\text{S}$; measured mass: 198.99271; error: 0.3 mDa) eluting at 2.81 min is a known OS, which has been characterized in previous work as 3-sulfooxy-2-hydroxy-2-methylpropanoic acid, a 2-methyl-

glyceric acid sulfate ester.¹⁰ Selected MS data (m/z 199 MS² and m/z 199 \rightarrow m/z 119 MS³) are given in Figures 4.2(F) and 4.2(G).

As in the case of deprotonated glycolic and lactic acid [Figs. 4.2(A) and 4.2(B)] the m/z 199 MS² spectrum is dominated by the bisulfate anion (m/z 97) [Fig. 4.2(F)]. Minor product ions are observed at m/z 181, 155 and 119, corresponding to the neutral loss of water, CO₂ and SO₃, respectively [Scheme 4.3(C)]. Furthermore, the further fragmentation of m/z 119 [Fig. 4.2(G)] can be readily explained, as outlined in Scheme 4.3(C).

In addition, there are two minor m/z 199 OSs eluting at RTs 3.85 and 4.65 min, which appear to be stereoisomers based on their very similar m/z 199 MS² and m/z 199 \rightarrow m/z 155 MS³ spectra [Figs. 4.2(H) and 4.2(K)]. Detailed interpretation of the MS data [Scheme 4.3(D)] leads us to tentatively assign these compounds to 2,3-dihydroxybutanoic acid OSs, with the sulfate group located at the 2-position. Accurate mass measurement supports that the first loss of 44 u from the deprotonated molecules corresponds to C₂H₄O. The 2,3-dihydroxybutanoic acid OSs can be explained by oxidation of the double bond of crotonaldehyde to a dihydroxy or epoxy derivative and subsequent sulfation of a hydroxyl or an epoxy group. Crotonaldehyde is a volatile organic compound that is known to have many sources, both biogenic and anthropogenic.³⁷

4.3.3. MW 184 organosulfates

The m/z 183 OS (C₄H₇O₆S; measured mass: 182.99728; error: 0.6 mDa) with RT 3.13 min corresponds to an unknown compound, which, to our knowledge, has not been reported in previous work. Selected LC/MS data are given in Figures 4.3(A) – 4.3(D). The m/z 183 MS² spectrum shows ions at m/z 165, 153, 139, and 97. The m/z 97 ion corresponds to the bisulfate anion (HSO₄⁻) and is consistent with an OS, whereas m/z 165 is due to the loss of a molecule of water and points to a free hydroxyl group, whereas m/z 153 can be explained by the loss of formaldehyde (CH₂O; 30 u), suggesting the presence of a terminal hydroxymethyl group.³⁶ Accurate mass data for the m/z 153 ion confirmed the loss of

formaldehyde [$\text{C}_3\text{H}_5\text{O}_5\text{S}$; measured mass: 152.98588; error: 0.7 mDa; Figure 4.3(D)]. Analysis of the DNPH-derivatives revealed a corresponding product and supported the presence of a carbonyl group in the unknown molecule. Selected LC/MS data for the DNPH derivative are presented in Figures 4.3(E) and 4.3(F). As the unknown MW 184 OS is probably related to isoprene or crotonaldehyde SOA, two possible structures containing a carbonyl group were considered for the unknown molecule, i.e., organosulfates of 2,3-dihydroxy-3-methylbutanal (**3** and **3'**) and 1,2-dihydroxy-3-butanone (**8** and **8'**), and an effort was made to synthesize both candidate molecules (Scheme 4.1). These molecules can be produced by further oxidation of the double bond of crotonaldehyde and methyl vinyl ketone to a dihydroxy or epoxy derivative and subsequent sulfation of a hydroxyl or an epoxy group.

Selected LC/MS data for the OSs of synthesized 2,3-dihydroxy-3-methylbutanal (**3** and **3'**, Scheme 1) and 1,2-dihydroxy-3-butanone (**8** and **8'**, Scheme 1) are given in Figures 4.4(A)–4.4(E) and Scheme 4.4(A), and Figures 4.4(F)–4.4(I) and Scheme 4.4(B), respectively. Comparison of these data with those obtained for the unknown MW 184 OS led us to assign the unknown molecule to 2-sulfooxy-1-hydroxybutan-3-one (**8'**). It is noted that there are some differences in the MS data, which can however be readily explained. The most notable difference is the appearance of the m/z 183 MS^2 spectra, where the bisulfate ion (m/z 97) is the base peak in the case of the synthesized molecule and rather weak (relative abundance 5%) in the case of the unknown molecule. A possible explanation is that the synthesized product also contains an isomeric co-eluting organosulfate of 3,4-dihydroxybutan-2-one with the sulfate group located at the terminal 4-position (1-sulfooxy-2-hydroxybutan-3-one), which could explain the formation of the abundant m/z 97 [Scheme 4.4(C)]. It thus appears that the location of the sulfate group strongly affects the abundance of m/z 97 in the isomeric mono-sulfate esters

of 3,4-dihydroxybutan-2-one. Further analysis of the LC/MS data obtained for the DNPH-derivative of the unknown MW 184 OS [Fig. 4(I)] also shows that this derivative results in diagnostic fragmentation with the m/z 363 MS^2 spectrum revealing a base peak at m/z 317, owing to the loss of 46 u that corresponds to the combined loss of a hydroxymethyl and a methyl group [Scheme 4.4(E)].

In a last step, we also confirmed the presence of 3,4-dihydroxybutan-2-one OS (**8'**) in an isoprene SOA sample that was analyzed in our previous study (results not shown).¹⁰ However, in that specific isoprene SOA sample the relative abundance of this MW 184 OS was much lower than in the ambient fine aerosol analyzed in the present study and was only about one-twentieth of that of the 2-methyltetrol-related OSs, providing an explanation as to why it escaped our attention.

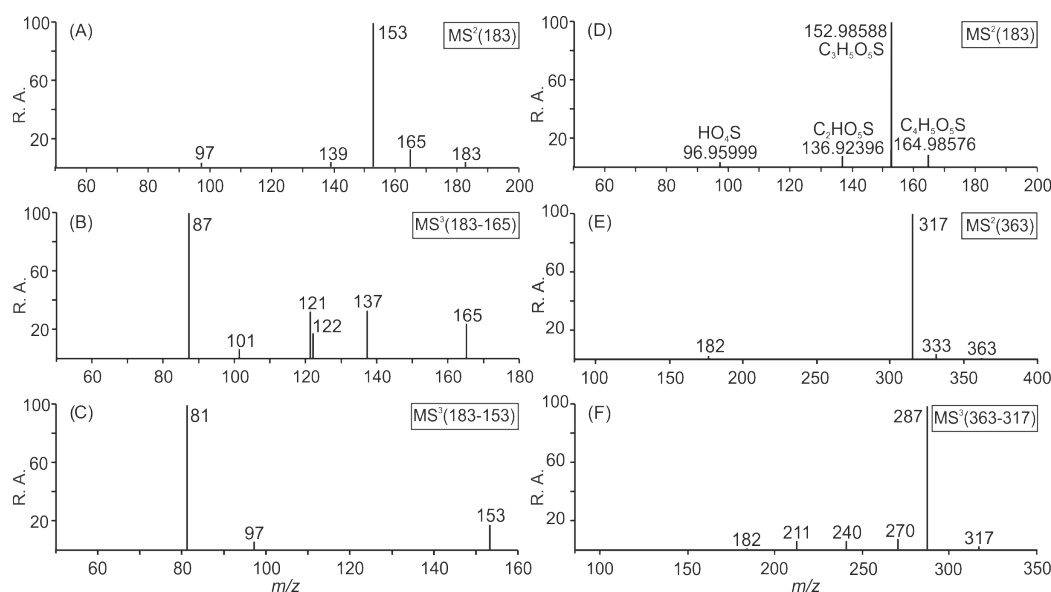


Figure 4.3. Selected LC/MS data (MS^2 and MS^3 product ion spectra) obtained for (A–D) the unknown organosulfate with a molecular weight of 184 and RT 3.13 min (Fig. 1), identified as 2-sulfooxy-3-hydroxybutan-3-one, and (E, F) its corresponding 2,4-dinitrophenylhydrazone derivative (RT 28.02 min). All MS data were obtained with the LXQ instrument, except the data shown in (D) which were obtained with the LTQ Orbitrap XL instrument.

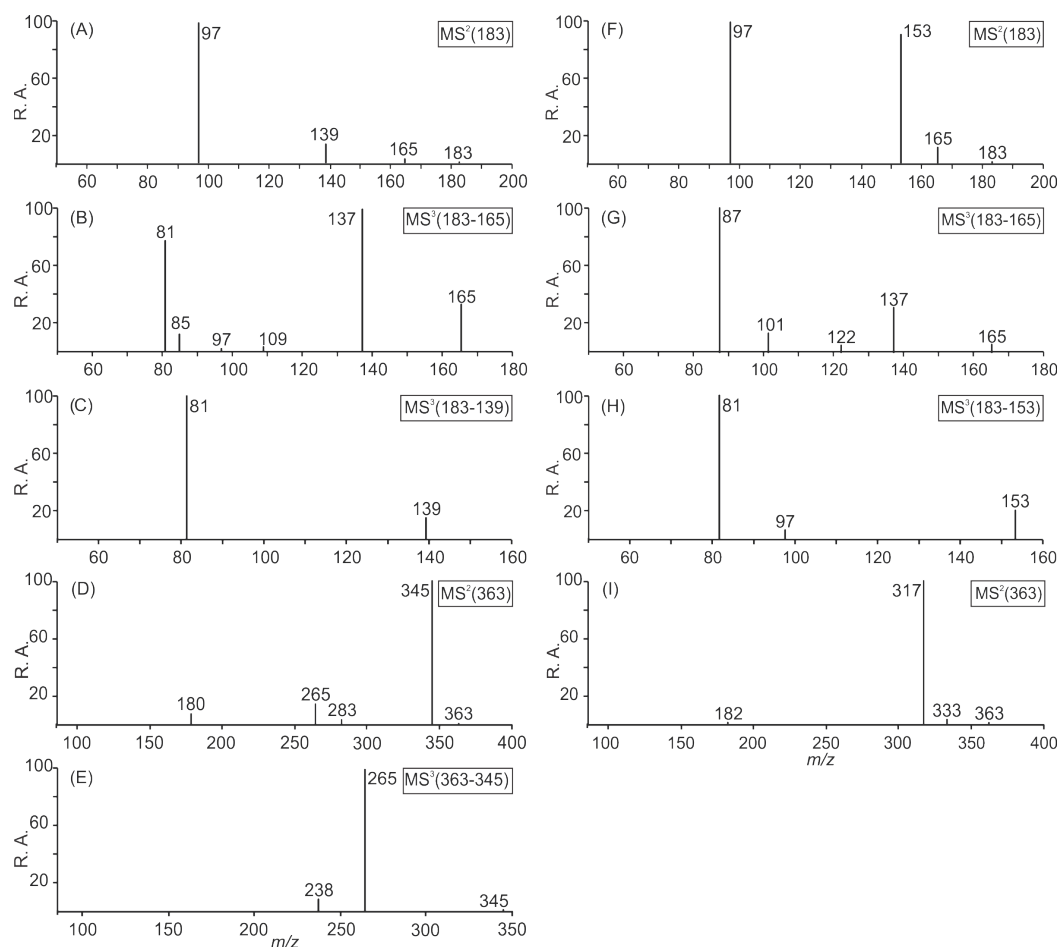
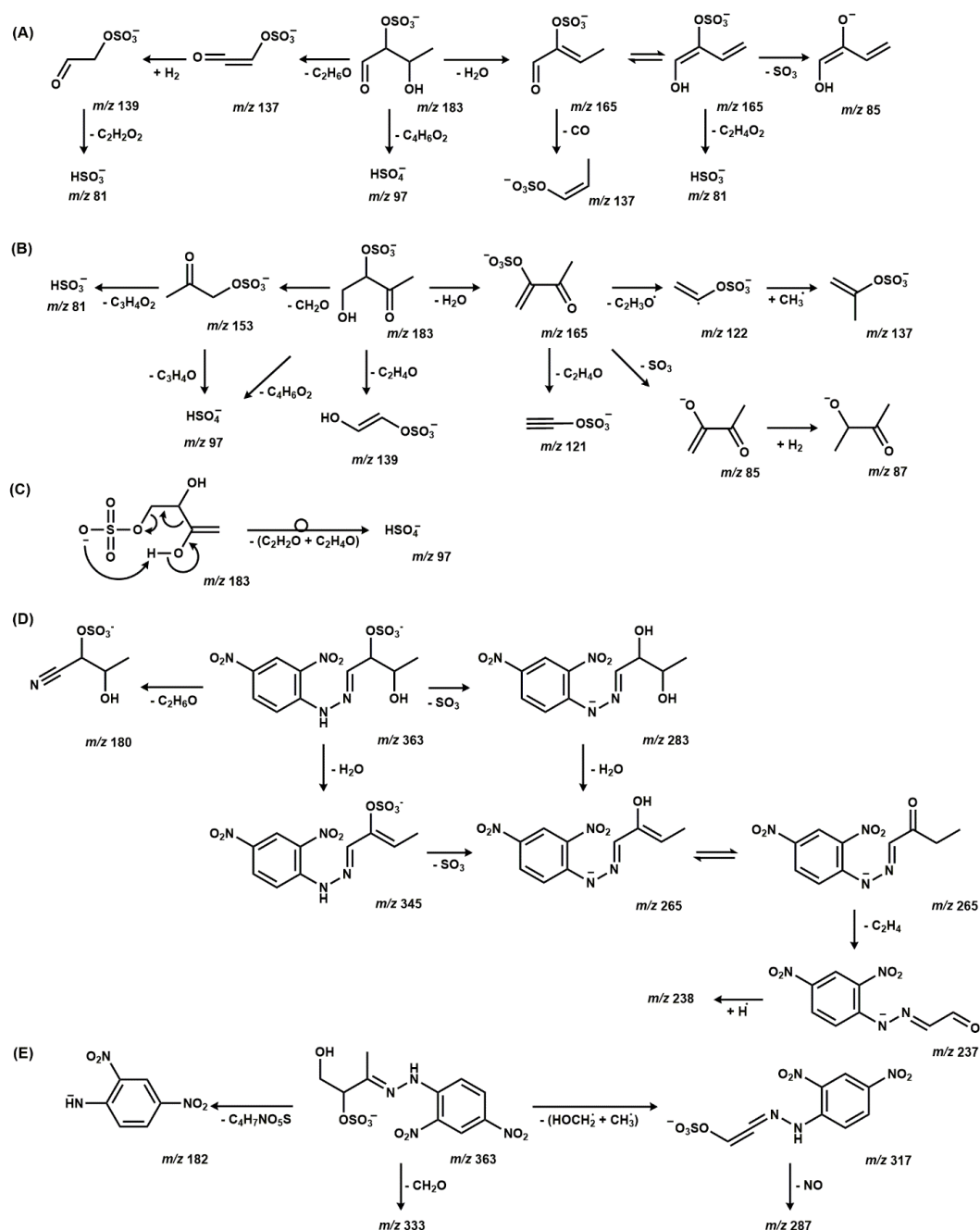


Figure 4.4. Selected LC/MS data (MS_2 and MS_3 product ion spectra) obtained for synthesized reference organosulfates with a MW of 184 and their corresponding 2,4-dinitrophenylhydrazone derivatives: organosulfates of (A–E) 2,3-dihydroxybutanal (**3** and **3'**, Scheme 1) and (F–I) 3,4-dihydroxy-2-butanone (**8** and **8'**, Scheme 4.1).



Scheme 4.4. Proposed fragmentation pathways for organosulfates related to (A) 2,3-dihydroxybutanal and (B, C) methyl vinyl ketone, and (D, E) their corresponding 2,4-dinitrophenylhydrazone derivatives. The structure shown in (C) represents the enol form of 1-sulfoxy-2-hydroxybutan-3-one.

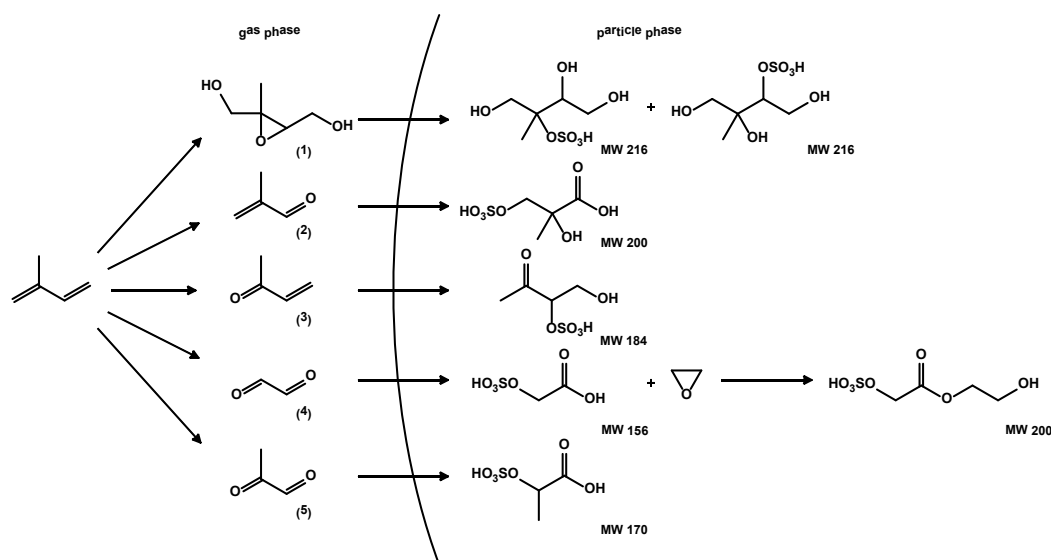
4.4. Conclusions

Detailed interpretation of LC/(–)ESI-MS data, including MS² and MS³ ion trap data and MS² Orbitrap data of the underivatized compounds and, in the case of the carbonyl-containing compounds, their DNPH-derivatives, and synthesis of reference compounds, led to a more complete structural characterization of polar organosulfates that are related to isoprene SOA and are present in ambient fine aerosols. In addition, the structures of minor MW 200 organosulfates could be related to crotonaldehyde, a biogenic volatile organic compound that has many sources, both biogenic and anthropogenic.

The fragmentation behavior of the targeted organosulfates indicated that the position of the organosulfate group affects the abundance of the bisulfate anion (m/z 97) as its formation competes with the neutral loss of small molecules such as CO₂, SO₃, formaldehyde (CH₂O), and oxirane or acetaldehyde (C₂H₄O). The diagnostic neutral loss of 30 u (CH₂O) allowed us to confirm a terminal hydroxymethyl group, whereas that of 44 u (CO₂ or C₂H₄O) supported the presence of carboxylic acid group (CO₂) or a terminal 2-hydroxyethyl or a glycolate ester group (C₂H₄O).

An important atmospheric implication is the presence of a polar organosulfate that has not been previously reported and is related to methyl vinyl ketone, which, together with methacrolein, is a major gas-phase oxidation product of isoprene.¹⁴ The further oxidation of methyl vinyl ketone could take place either in the gas or particle phase and additional research is required to establish the formation pathways leading to the 2-sulfooxy-1-hydroxybutan-3-one. A photochemical formation mechanism of organosulfates is, however, likely in view of the results of previous studies.^{29,34,37-40} With respect to the methacrolein- and methyl vinyl

ketone-related OSs, for example, it would be relevant in future research to evaluate whether they could be generated in the aqueous aerosol phase through the action of sulfooxy radical anions³⁸ or follow the recently reported new epoxide formation mechanism via catalytic oxidation of alkenes by air with α -dicarbonyls as photosensitizers.³⁴ The structures of abundant organosulfates other than the MW 184 compound have been confirmed and/or revised as organosulfate esters of glycolic acid (MW 156), lactic acid (MW 170), and glycolic glycolate (MW 200). In summary, additional insights have been obtained on isoprene SOA-derived polar organosulfates and possible formation pathways (Scheme 4.5). However, except for the formation of the C₅-epoxydiol-related OSs (2-methyltetrol OSs; MW 216),^{11,13} there are still insufficient insights into the detailed formation mechanisms leading to the other isoprene-related OSs.



Scheme 4.5. Overview of the organosulfates related to the following gas-phase oxidation products of isoprene: (1) C₅-epoxydiol; (2) methacrolein; (3) methyl vinyl ketone; (4) glyoxal; and (5) methyl glyoxal.

4.5. References

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CHAPTER 5

Ion-pairing liquid chromatography/negative ion mass spectrometry for improved analysis of polar isoprene-related organosulfates

Adapted from:

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5.1. Introduction

Fine particulate matter from vegetated areas contains as important constituents polar organosulfates, which are related to SOA from the photooxidation of isoprene.¹⁻⁵ These polar OSs are of climatic relevance owing to their hydrophilic properties, which enhance the capacity of the aerosols to serve as cloud nucleation nuclei. Negative ion electrospray ionization mass spectrometry is well suited for the sensitive detection of organosulfates because the sulfate group is readily deprotonated during the ionization process. However, the LC/(–)ESI-MS analysis of polar OSs using RP-LC on C₁₈-based columns poses analytical challenges, which are connected to the polarity and the ionic character of the compounds and their co-occurrence with ammonium sulfate. LC retention and partial separation of the polar isoprene-related OSs, with, as major compounds, sulfate esters of 2-methyltetrols (MW 216), 2-methylglyceric acid (MW 200), and 1,2-dihydroxy-3-butanone (MW 184), have been achieved using di- or trifunctionally bonded C₁₈-based stationary phases.¹⁻⁵ Hydrophilic interaction chromatography using a silica column has also been applied for the LC/(–)ESIMS analysis of polar OSs;^{6,7} as in the case of di- and trifunctionally C₁₈-bonded stationary phases, limited retention and separation of OSs could be obtained. Ion-pairing LC/(–)ESI-MS methods have been shown to offer a suitable approach to the analysis of very polar organophosphate drug metabolites, which, like the targeted OSs, are highly polar and ionic, in biological fluids.⁸⁻¹⁰ In addition, in previous work we have successfully applied ion-pairing LC/(–)ESI-MS to the analysis of methane-sulfonate in marine aerosol samples.¹¹ In the present work, we have evaluated an ion-pairing LC/(–)ESI-MS method using dibutylammonium acetate with the aim of improving the separation of the above-mentioned isoprene-related polar OSs and sulfate. We demonstrate the usefulness of the ion-pairing LC/(–)ESI-MS method to the separation of polar OSs from fine biogenic aerosol.

5.2. Experimental section

5.2.1. Chemicals

Acetonitrile (HPLC supra-gradient grade) used as LC mobile phase and methanol (ULC/MS grade) used for sample preparation were from Biosolve NV (Valkenswaard, The Netherlands), and the ion-pairing reagent dibutylammonium acetate (0.5 mol/L in water; for LC/MS) was from TCI (Tokyo, Japan). D-Galactose-6-sulfate sodium salt (purity >98%) was from Sigma-Aldrich (St. Louis, MO, USA); methanesulfonic acid (purity >99%), ethanesulfonic acid (purity >95%), and 2-propanesulfonic acid sodium salt monohydrate (purity >99%) were from ACROS (Geel, Belgium). High-purity water (18.2 MΩ·cm; total organic carbon: 2 ppb) used to prepare the aqueous LC mobile phase and reconstitute aerosol extracts was supplied by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

5.2.2. Aerosol samples and sample preparation

Archived PM_{2.5} aerosol samples collected from K-puszt, Hungary, during a 2006 summer campaign were used. Details about the aerosol sample collection and sample processing are given in Section 4.2.2. A fraction of the residue from a pooled sample containing 570 mg of OC was redissolved in 1.5 mL of methanol/water (1:4; v/v) by first dissolving the fraction in 0.3 mL of methanol and then adding 1.2 mL of water. For the analysis of the ambient sample, the IP reagent was placed in the injection solution by adding 10 mL of 0.5 mol L⁻¹ DBAA to 90 mL of the above reconstituted sample.

5.2.3. Liquid chromatography

Use was made of IP RP-LC with a C₁₈ Hypersil GOLD column. See Chapter 3, Section 3.5.1 for further details.

5.2.4. Mass spectrometry

A linear ion trap mass spectrometer (LXQ, Thermo Scientific) was used in this work, for the operation conditions, see Chapter 3, Section 3.6.3.

For comparison, the ambient sample was also analyzed using regular RP-LC with a C₁₈ T3 column (2.1×150 mm, 3 mm; Waters, Milford, MA, USA), as employed in previous work (see Section 4.2). The isoprene SOA-related OSs in the ambient sample were assigned based on comparison of their $[M - H]^-$ MS² product ion spectra with those previously reported.^{3,5}

5.3. Results and discussion

A mixture of four commercially available compounds including three organosulfonates as surrogate compounds for organosulfates, i.e., methanesulfonate (MSA), ethanesulfonate (ES), 2-propanesulfonate (PS), and D-galactose-6-sulfate (GS), was employed to develop the ion-pairing LC/MS method for the analysis of small polar organosulfates. In a first series of experiments, only the IP reagent was used in the mobile phase and methanol was compared with acetonitrile as mobile phase (B). Satisfactory RTs for the test compounds were obtained with acetonitrile but were too long with methanol; using acetonitrile the RTs were 3.35, 3.40, 3.64, and 5.20 min for GS, ES, MSA, and PS, respectively. However, using this system peak broadening was observed for GS. In a second series of experiments, the IP reagent was added to the injection mixture, which resulted in satisfactory peak shapes for the four test compounds [Fig. 5.1(A)]. Adding the IP reagent directly to the reconstitution solution has been reported to be successful in the ion-pairing LC/MS analysis of an organophosphate drug metabolite.¹⁰ We further evaluated whether satisfactory peak shapes could still be achieved upon omitting the IP reagent from the mobile phase. However, this approach led to co-elution of the three sulfonic acids (RT 3.42 min), although with satisfactory peak shape, and a poor peak shape for GS (RT 3.31 min). Hence, further work was

performed with the IP reagent being present both in the mobile phase and in the reconstitution solution. Thus, for the highest amount of each of the test compounds injected on column in a volume of 5 mL the molar excess of DBAA was more than 103 (i.e., 3.3×10^3 , 4.1×10^3 , 8.2×10^3 , and 4×10^3 for 1.46 ng MSA, 1.34 ng ES, 0.75 ng PS, and 1.03 ng GS). Because a constant amount of IP reagent was present in the mobile phase as well as in the injection solution, no shift in RT was observed when the injection volume was changed, as reported for the ion-pairing LC/MS analysis of an organophosphate drug metabolite.¹⁰ To evaluate the sensitivity of the ion-pairing LC/MS method, standards at seven concentrations spanning the range 0.002 ng to 1.5 ng mL⁻¹ were prepared and an aliquot of 5 µL was injected.

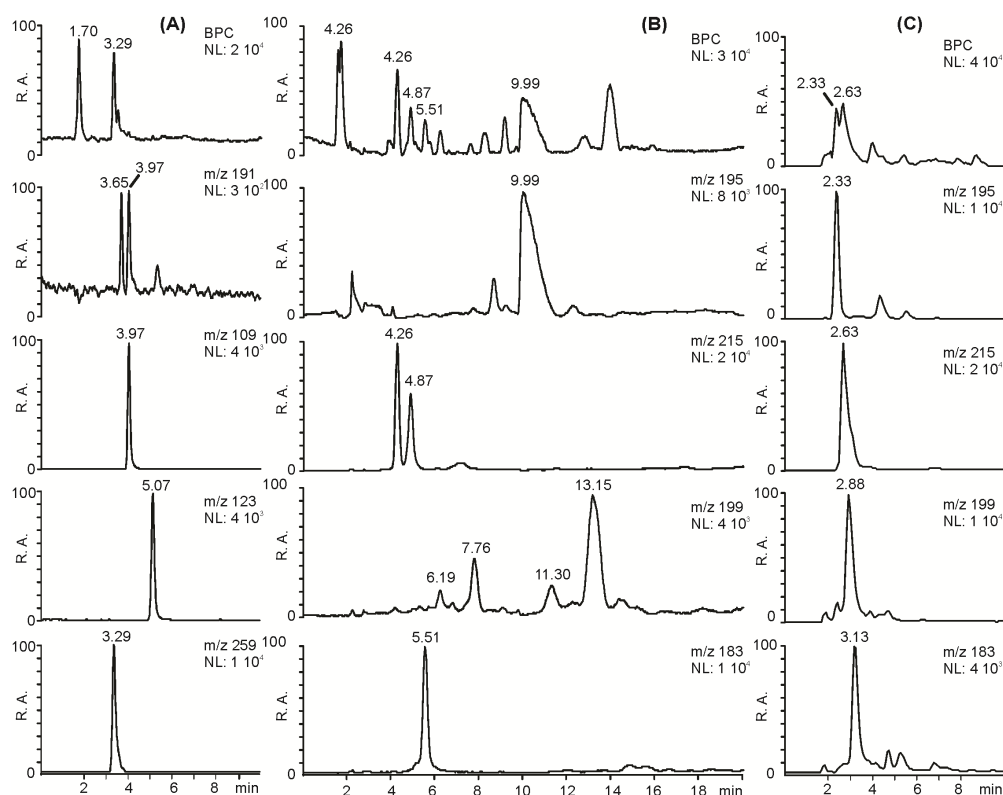


Figure 5.1. Selected LC/(-)ESI-MS chromatographic data (i.e., BPCs and EICs) for (A) a test mixture containing methanesulfonate (8.3 ng) (m/z 191), ethanesulfonate (10.3 ng) (m/z 109), 2-propylsulfonate (20.5 ng) (m/z 123), and D-galactose 6-sulfate (10 ng) (m/z 259) analyzed with the developed ion-pairing method; (B) K-pusztá fine aerosol containing sulfate (m/z 195) and sulfate esters of 2-methyltetrols (m/z 215), 2-methylglyceric acid (m/z 199), and 1,2-dihydroxy-3-butanone (m/z 183) analyzed with the same ion-pairing method as for (A); and (C) the same K-pusztá fine aerosol analyzed with a method previously reported using a C_{18} T3 column.⁵ The MW 200 compounds eluting at 6.19 and 7.76 min (B) could not be firmly assigned to OSs, because of ambiguous m/z 199 \rightarrow m/z 181 MS^3 product ion data revealing the absence of a m/z 97 bisulfate anion.

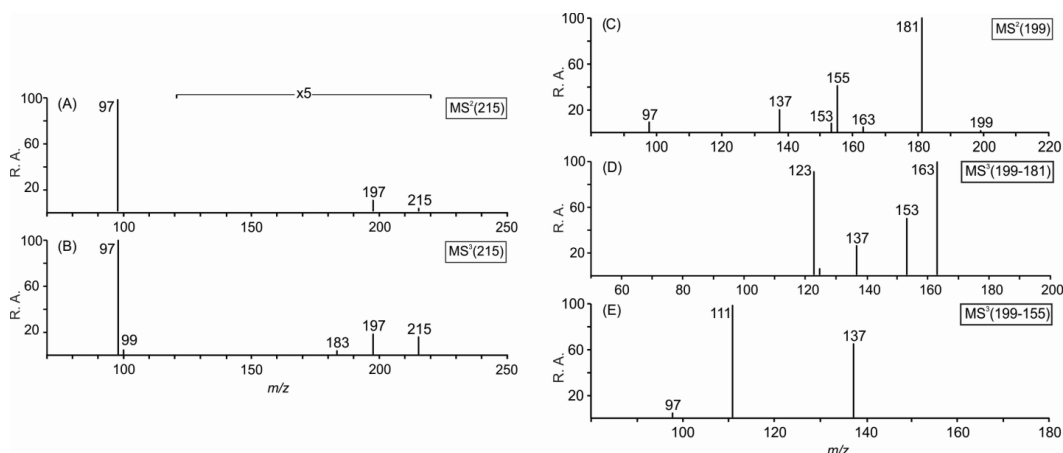


Figure 5.2. (A, B) Selected MS² product ion spectra data for the deprotonated forms of separated 2-methyltetrol OSs with RTs 4.26 min (A) and 4.87 min (B), which were assigned to erythro and threo isomers, respectively, and (C–E) selected MS² and MS³ product ion spectra data for the deprotonated form of an unknown MW 200 OS with RT 11.30 min, which was tentatively assigned to an OS of 1,3,4-pentanetriol with the sulfate group located at the 3-position.

The test compounds could be detected with a signal-to-noise ratio of about 10 for an amount injected on column of 3.7 ng, 0.04 ng, 0.03 ng, and 0.02 ng, for MSA, ES, PS, and GS, respectively, demonstrating the sensitivity of the method.

Figure 5.1(A) shows selected LC/MS data obtained for a standard mixture (corresponding to 8.3 ng, 10.3 ng, 20.5 ng, and 10 ng injected on column for MSA, ES, PS, and GS, respectively), including a BPC and EICs at m/z 191, 109, 123, and 259, corresponding to an adduct ion of methanesulfonate (i.e., $\text{CH}_3\text{SO}_3\text{H}:\text{CH}_3\text{SO}_3^-$), ethanesulfonate, 2-propanesulfonate, and D-galactose-6-sulfate, respectively. It can be seen that ethanesulfonate (m/z 109) is also detected on the m/z 191 trace, owing to the formation of an adduct ion with sodium acetate (82 Da) which is present in the system (acetate is the anionic part of the IP reagent).

In a following step, the method was applied to an ambient aerosol sample, i.e., an extract of K-pushta fine aerosol containing polar organosulfates, which was

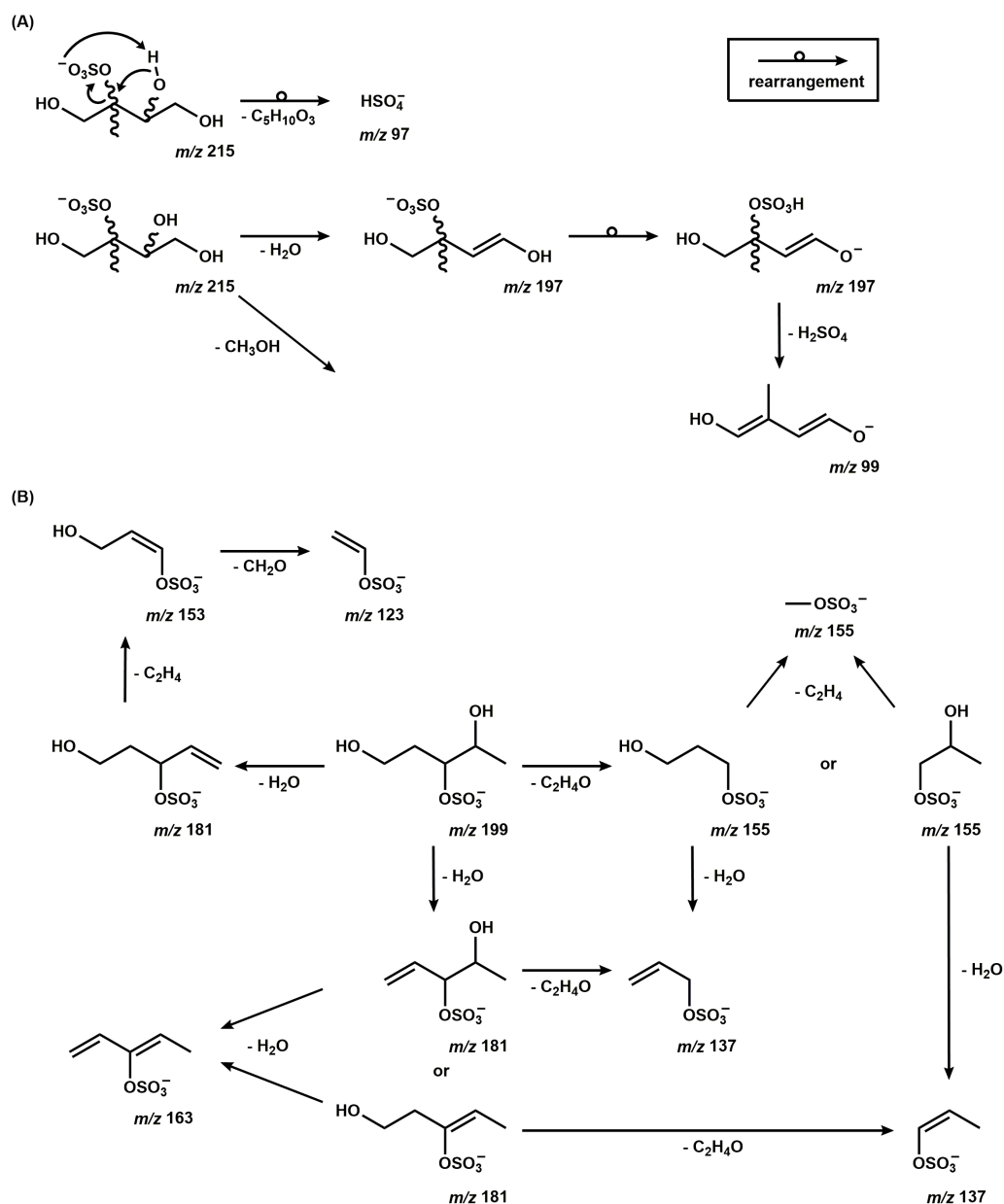
investigated in detail in a recent study.⁵ Figure 5.1 presents the comparison of selected LC/MS data for K-pusztta fine aerosol obtained with the developed ion-pairing method [Fig. 5.1(B)] and the method using the T3 column [Fig. 5.1(C)]. BPCs and EICs at m/z 195, 215, 199 and 183, corresponding to sulfate and abundant OSs that are related to isoprene SOA, are shown. It can be seen that the ion-pairing method provides better retention for the targeted OSs [i.e., OSs of 2-methyltetrols (m/z 215), 1,2-dihydrobutan-3-one (m/z 183), and 2-methylglyceric acid (m/z 199)] than the method based on the T3 column, where the 2-methyltetrol OSs are only partially separated from sulfate and 2-methylglyceric acid OS. Sulfate (RT 9.99 min) elutes as a broad tailing peak after the OSs of the 2-methyltetrols (m/z 215) (RTs 4.26 and 4.87 min), which are baseline-separated, and a 1,2-dihydroxy-3-butanone OS containing the sulfate group at the 1-position (m/z 183) (RT 5.51 min). Furthermore, a better chromatographic separation of m/z 199 OSs could be achieved than in the T3 method with the major compound, 2-methylglyceric acid OS containing the sulfate group at the terminal position (RT 13.15 min) being separated from other m/z 199 compounds, although 2-methylglyceric acid OS elutes as a quite broad peak. This improved chromatographic separation enabled a more detailed mass spectral characterization of the 2-methyltetrol OSs and the characterization of a relatively abundant m/z 199 OS (RT 11.30 min) which was not revealed with the T3 method, owing to co-elution.

Figure 5.2 shows selected mass spectral data for the separated 2-methyltetrol OSs [Figs. 5.2(A) and 2(B)] and the m/z 199 OS eluting at 11.30 min [Figs. 5.2(C)–5.2(E)]. Based on GC/MS analysis with prior trimethylsilylation of similar K-pusztta aerosol samples, it is known that the 2-methyltetrols occur as a mixture of diastereoisomers with a threo/erythro ratio of approximately 2:5.¹² Taking this information into account, the elution order of the 2-methyltetrol OSs upon ion-

pairing LC is determined as erythro - threo. As expected for diastereoisomers, only small differences in the relative abundance (RA) of certain product ions can be seen. It is noted that the RA of the m/z 215 precursor ion in the MS² product ion spectra is the highest for the later-eluting threo isomer, consistent with a slightly higher stability of the deprotonated form of the threo isomer than of the erythro isomer upon collisional activation in the ion trap. Limited information can be inferred regarding the position of the sulfate group, which is probably present at the 3-position, taking into account the formation mechanism of the 2-methyltetrol OSs through sulfation of C₅-epoxydiols.⁴ However, the presence of product ions at m/z 183 and 199 is consistent with a sulfate group at the 2-position. Based on detailed interpretation of the mass spectral data (Scheme 5.1), the m/z 199 OS eluting at 11.30 min could be tentatively assigned to an OS of 1,3,4-pentanetriol with the sulfate group located at the 3-position. The biogenic precursor of this MW 200 organosulfate is probably 3-pentene-1-ol, a known plant volatile,^{13,14} but further research is needed to support its atmospheric origin.

5.4. Conclusions

In conclusion, compared with a previous method based on the use of a C₁₈ T3 column the developed ion-pairing LC/(–)ESI-MS method allows an improved chromatographic separation of polar organosulfates, and, hence, their more detailed mass spectral characterization.



Scheme 5.1. Proposed fragmentation pathways for the deprotonated forms of (A) 2-methyltetrol OSs (RTs 4.26 and 4.87 min) and (B) the unknown MW 200 OS (RT 11.30 min), tentatively assigned to an OS of 1,3,4-pentanetriol with the sulfate group located at the 3-position.

5.5. References

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CHAPTER 6

Characterization of polar organosulfates in secondary organic aerosol from the green leaf volatile 3-Z-hexenal

Adapted from:

Shalamzari, M. S., Kahnt, A., Vermeylen, R., Kleindienst, E. T., Lewandowski, M., Cuyckens, F., Maenhaut, W., Claeys, M.: Characterization of polar organosulfates in secondary organic aerosol from the green leaf volatile 3-Z-hexenal. *Environ. Sci. Technol.* **2014**, 48, 12671-12678.

6.1. Introduction

Much information is available about SOA formation from terpenes, including mono- and sesquiterpenes, and isoprene [for a review, see Hallquist et al., 2009]¹. However, information about SOA formation from green leaf volatiles, an important class of biogenic volatile organic compounds, is very scarce. To our knowledge, only SOA formation from the GLVs 2-*E*-hexenal and 3-*Z*-hexenyl acetate has been examined.²⁻⁴ In a previous study, we presented evidence that a polar organosulfate related to the C₅-plant volatile, 2-pentenal, which is a photolysis product of 3-*Z*-hexenal,⁵ occurs in ambient fine aerosol from a forested site, i.e., K-pusztá, Hungary; more specifically, a sulfate ester of 2,3-dihydroxypentanoic acid could be identified using LC/(-)ESI-MS and detailed interpretation of the MS data.⁶ Here, we provide evidence that the unsaturated aldehydic GLV, 3-*Z*-hexenal, is a potential precursor for biogenic SOA through formation of organosulfates.

A small number of VOCs are naturally released from plants such as isoprene and terpenes. However, many more VOCs are emitted when plants are wounded or attacked by insects. The chemical characteristics of these VOCs differ with the plant species and with the herbivorous insect species, and both parasitic and predatory insects, natural enemies of herbs, are attracted by these volatiles.^{7,8} GLVs also have a potential role in tropospheric chemistry as they may serve as precursors for ozone and SOA.⁹ 3-*Z*-hexenal is an important GLV formed in green leaves from the cell membrane unsaturated fatty acid α -linolenic acid by the combined reaction of lipoxygenase and hydroperoxide lyase enzymes.¹⁰ It is known to preferentially react in the atmosphere during daytime through reaction with the OH radical and to a lesser extent with ozone.^{11,12}

Organosulfate formation has been well documented for SOA from the photooxidation of isoprene^{6,13-16} and proceeds via sulfation of intermediary epoxy

derivatives^{15,17,18} or reaction of first-generation oxidation products (i.e., methacrolein and methyl vinyl ketone) with the sulfate anion radical.¹⁹⁻²² The most abundant isoprene-related OSs in ambient fine aerosol from forested sites during summer are sulfate esters of the 2-methyltetrols.^{14,23} Similar to the polar OSs related to SOA from the photooxidation of isoprene, those originating from the photooxidation of unsaturated aldehydes may also be hydrophilic and substantially contribute to the total SOA budget. Polar OSs are of climatic interest due to their capability to enhance the hydrophilic properties of the aerosol, and, hence, their cloud-forming properties.²⁴ Furthermore, the novel OSs are potential marker compounds for SOA formation occurring under acidic conditions by particle-phase reactions with sulfuric acid,²⁵ formed by oxidation of sulfur dioxide, which is mainly from anthropogenic origin in continental regions of the globe.²⁶

In the present study, we have investigated organosulfate formation from 3-Z-hexenal by conducting smog chamber experiments in the presence of acidic ammonium sulfate seed aerosol and have focused on the structural characterization of MW 226 OSs, which are also present at a substantial relative abundance in ambient fine aerosol. In addition, attention was given to the chemical characterization of abundant MW 212 OSs, which are lower homologs of the MW 226 3-Z-hexenal-related OSs but whose biogenic precursor(s) remain(s) to be identified. Abundant MW 212 OSs have been noted in earlier studies dealing with the chemical characterization of OSs or biogenic SOA but are largely unknown so far.^{6,14,23,27} Both MW 226 and 212 OSs have been quantified in PM_{2.5} samples from Brasschaat, Belgium, and their median concentrations were estimated at 6.5 and 4.6 ng m⁻³, comparing quite favorably to that of 6.4 ng m⁻³ determined for the isoprene-related MW 216 OSs and, thus, suggesting that they have a similar magnitude.²³ Two different LC techniques were employed to

separate the polar OSs: the first technique uses a reversed-phase trifunctionally-bonded C₁₈ stationary phase,¹⁶ whereas the second technique is based on ion-pairing C₁₈ LC using dibutylammonium acetate as the IP reagent. The latter technique has recently been applied to polar isoprene SOA-related OSs and has been shown to provide an improved chromatographic separation for isomeric and isobaric compounds compared to the first technique using a trifunctionally-bonded C₁₈ phase.²⁸

6.2. Experimental section

6.2.1. Chemicals

Methanol (ULC/MS grade) used for sample preparation and as LC mobile phase and acetonitrile (HPLC supra-gradient grade) were purchased from Biosolve NV (Valkenswaard, The Netherlands); the IP reagent DBAA (0.5 mol/L in water; for LC/MS) was from TCI (Tokyo, Japan); and *cis*-pinonic acid (purity: 98%; for MS signal optimization) was from Sigma-Aldrich (St. Louis, MI, USA). High-purity water (resistivity, 18.2 MΩ cm; total organic carbon, 2 ppb) used for redissolving aerosol extracts and preparing the aqueous LC mobile phase was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). 3-Z-hexenal (50% solution in triacetin) used for chamber experiments was from Sigma-Aldrich.

6.2.2. Aerosol samples

6.2.2.1. Laboratory SOA samples

The experimental conditions for the 3-Z-hexenal chamber experiments used in the present study are summarized in Table 1. For details about the experimental conditions, see Chapter 3, Section 3.3. For details about the sample preparation, see Chapter 3, Section 3.4.

6.2.2.2. Ambient fine aerosol

See Chapter 3, Sections 3.2 and 3.4.

In the case of ion-pairing LC/MS, the IP reagent was placed in the injection solution by adding 10 μL of 0.5 mol L^{-1} DBAA to 90 μL of the redissolved sample. Afterwards, the sample was analyzed with LC/(-)ESI-MS using an aliquot of 5 μL .

Table 6.1. Experimental conditions for experiments used for the structural characterization of unknown organosulfates related to 3-Z-hexenal SOA.^a

Sample code	ER627– GF6		ER627– GF10	
	Initial:	Steady State:	Initial:	Steady State:
Hydrocarbon concentration (ppm of C)	2.3	0.02	2.2	0.02
NO_x ^b concentration (ppb)	290	117	290	200
O_3 concentration (ppb)		265		280
OC concentration (ppb)		9		5
Seed type concentration ($\mu\text{g m}^{-3}$)	SA 30 $\mu\text{g m}^{-3}$		$\frac{1}{2}$ AS + $\frac{1}{2}$ SA 30 $\mu\text{g m}^{-3}$	
Other Conditions	4 light banks 1079 nmol m^{-3} $[\text{H}^+]$ air, RH of 29%		4 light banks 439 nmol m^{-3} $[\text{H}^+]$ air, RH of 29%	

^aSA, sulfuric acid; AS, ammonium sulfate; and RH, relative humidity. ^bAll of the initial NO_x was NO.

6.2.3. Liquid Chromatography/Mass Spectrometry

6.2.3.1. Liquid Chromatography

Use was made of both regular RP-LC with an Atlantis T3 column and of IP RP-LC with a Hypersil GOLD column. See Chapter 3, Section 3.5.1 for further details.

6.2.3.2. Mass spectrometry

A linear ion trap mass spectrometer (LXQ, Thermo Scientific) was used in this work; for the operation conditions, see Chapter 3, Section 3.6.3.

Accurate mass measurements were carried out using an LTQ-Orbitrap mass spectrometer (Thermo Scientific), equipped with a Waters Alliance 2695 HPLC system (Waters, Milford, Massachusetts, USA). The LTQ Orbitrap mass spectrometer was equipped with an ESI source operated in the negative ion mode under the same conditions as described above for the ion-trap experiments. The source parameters were tuned for maximum sensitivity using a 50 $\mu\text{g mL}^{-1}$ malic acid standard solution. The mass resolution was set at 100000 in the MS¹ mode and 7500 in the MS² and MS³ modes. For MS² and MS³ experiments, an isolation width of 5 m/z units and a normalized collision energy level of 35% were applied. The accurate mass measurements were obtained using external calibration, providing a mass accuracy better than 1 mDa. The accurate mass measurements were only carried out for K-pusztá PM_{2.5} aerosol analyzed with RP-LC for selected peaks. Data were acquired and processed using Xcalibur 2.0 software.

6.3. Results and discussion

Figure 6.1 shows selected LC/MS chromatographic data using regular RP-LC obtained for K-pusztá fine aerosol, including a BPC and EICs, which correspond to the deprotonated forms of OSs related to isoprene (m/z 215), (an) unknown BVOC precursor(s) (m/z 211), and 3-Z-hexenal (m/z 225). Of these, the m/z 215 isoprene SOA-related OSs have been identified in previous studies as sulfate

esters of 2-methyltetrols,^{6,13-15} which are formed by sulfation of intermediary C₅-epoxydiols.¹⁵ The LC/MS chromatographic data reveal that the targeted OSs at *m/z* 225 and 211 have a relative abundance (on the basis of signal intensities) comparable to the *m/z* 215 compounds. It has already been demonstrated in a previous study that the *m/z* 215 isoprene-related OSs could be resolved in two peaks with the ion-pairing RP-LC technique;²⁸ with the latter technique an improved separation could also be obtained for the *m/z* 225 and 211 OSs, as will be illustrated in the following two sections. Figure 6.1 also shows selected LC/MS chromatographic data for 3-Z-hexenal SOA [sample ER627-GF10 (Table 1)] using the RP-LC technique; comparable results were obtained for sample ER627-GF6 (results not shown).

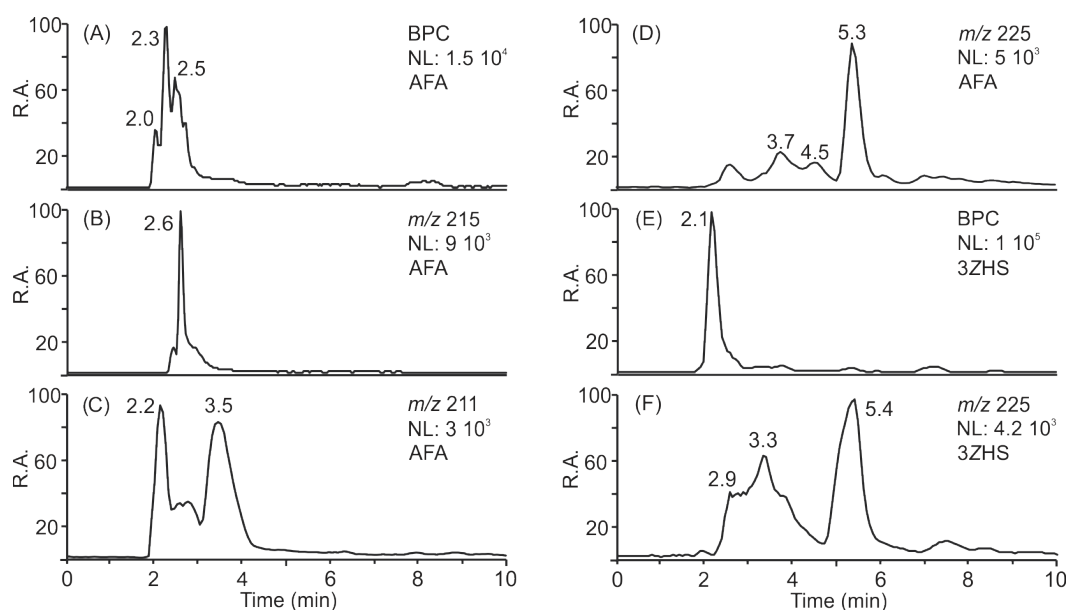


Figure 6.1. Selected LC/MS chromatographic data using regular RP-LC obtained for (A–D) ambient fine aerosol and (E and F) 3-Z-hexenal SOA, including a BPC and EICs, corresponding to the deprotonated forms of OSs related to isoprene (m/z 215), 3-Z-hexenal (m/z 225), and (an) unknown biogenic volatile organic compound precursor(s) (m/z 211). The m/z 211 EIC for 3-Z-hexenal is not included because no peaks corresponding to those observed for ambient fine aerosol could be seen with the IP RP-LC technique. AFA, ambient fine aerosol; NL, normalization level; and 3ZHS, 3-Z-hexenal SOA.

6.3.1. Structural characterization of MW 226 organosulfates related to 3-Z-hexenal

It can be seen from Figure 6.1 (m/z 225 EIC) that there are several unresolved peaks eluting between 2 and 6 min, of which the major peak ($C_6H_9O_7S$; measured mass, 225.00809; error, +0.6 mDa; K-pushta fine aerosol) eluting at a RT of 5.3 min is present in 3-Z-hexenal SOA (RT of 5.4 min); hence, the m/z 225 OSs can be related to 3-Z-hexenal. Selected MS data (MS^2 and MS^3) for the major peak are given in panels A–D of Figure 6.2. Additional MS data for the early eluting m/z 225 compounds are presented in Figure 6.3. Panels E and F of Figure 6.2 illustrate that the IP RP-LC technique provides a separation of the m/z 225 isomers. It can

be noted that there is a difference in the chromatographic profiles: ambient fine aerosol reveals a more complex pattern with at least six isomers, whereas 3-Z-hexenal shows four distinct isomers with corresponding RTs. A possible explanation for the more complex m/z 225 isomeric pattern of ambient fine aerosol could be the presence of isomers originating from 2-Z-hexenal, which is a commonly occurring plant leaf volatile.¹⁰ The differences in the relative abundances of characteristic ions in the spectra for the early eluting m/z 225 isomers in RP-LC (Fig. 6.3) are also likely due to a different isomeric pattern between ambient fine aerosol and 3-Z-hexenal SOA. Detailed interpretation of the MS data allows the assignment of the m/z 225 OSs to isomeric forms of sulfate esters of 3,4-dihydroxyhex-5-enoic acid, with the sulfate group located at the C-3 or C-4 position [Scheme 6.1(A)]. The presence of the bisulfate (HSO_4^-) ion (m/z 97) in both the MS^2 and MS^3 spectra (Fig. 6.2) is consistent with an organosulfate,^{6,13–16,30,31} whereas the loss of CO_2 (44 u) upon fragmentation of the precursor ion (m/z 225), affording m/z 181, indicates a carboxyl group. Other diagnostic fragmentations include the loss of 44 u ($\text{C}_2\text{H}_4\text{O}$, m/z 137) from one of the m/z 181 isomeric forms [right of Scheme 6.1(A)], pointing to a terminal 1-hydroxyethyl group,¹⁶ as well as the further loss of 28 u (C_2H_4 , m/z 153) from both m/z 181 isomeric forms, consistent with a terminal ethylene group. It is worth noting that the m/z 225 \rightarrow 181 MS^3 spectrum obtained for ambient fine aerosol shows an abundant m/z 181 precursor ion, whereas the latter ion is completely fragmented upon MS^3 in the case of 3-Z-hexenal SOA, consistent with the observation that ambient fine aerosol shows a more complex m/z 225 EIC profile upon IP RP-LC. The detection of multiple isomers in 3-Z-hexenal SOA upon IP RP-LC is in agreement with the structural proposal because the two positional isomers with the sulfate group positioned at C-3 or C-4 each can occur as diastereoisomeric pairs.

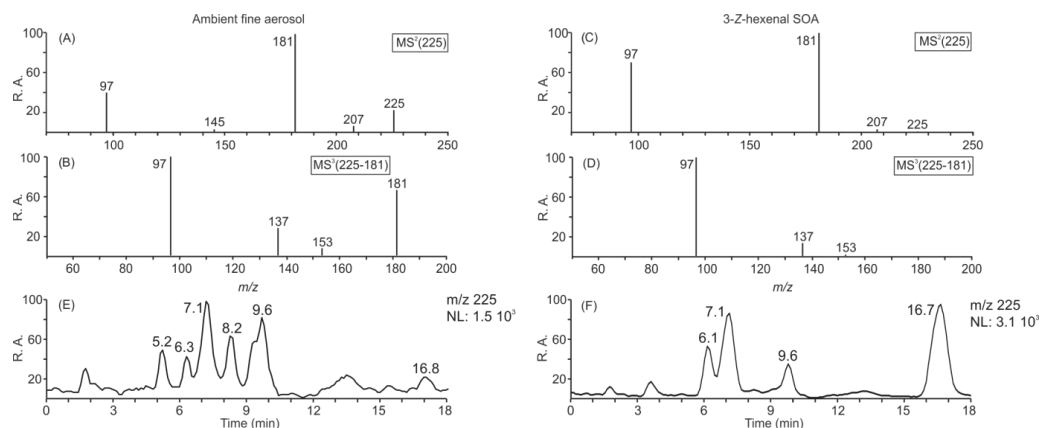


Figure 6.2. Selected MS data (MS^2 or MS^3 product ion spectra) obtained with the regular RP-LC technique for (A, B) the compounds eluting at 5.3 min for ambient fine aerosol and (C, D) the compounds eluting at 5.4 min in 3-Z-hexenal SOA (Fig. 1; m/z 225 EIC). LC/MS chromatographic data (m/z 225 EICs) obtained with the ion-pairing RP-LC technique for (E) ambient aerosol and (F) 3-Z-hexenal SOA.

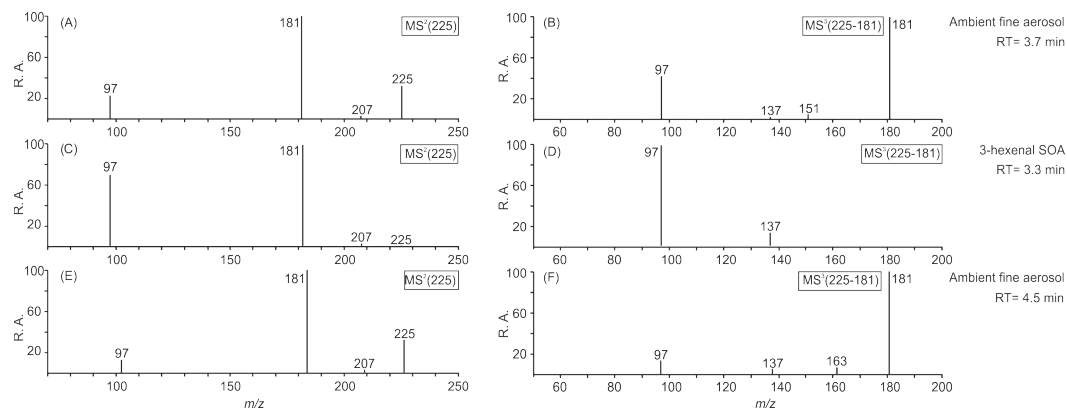


Figure 6.3. MS^2 and MS^3 product ion data obtained for ambient fine aerosol and 3-Z-hexenal SOA using the regular RP-LC technique (panels D and F of Fig. 6.1) for the m/z 225 compounds eluting at RTs 3.3, 3.7 and 4.5 min before the major peak at 5.3 and 5.4 min, respectively.

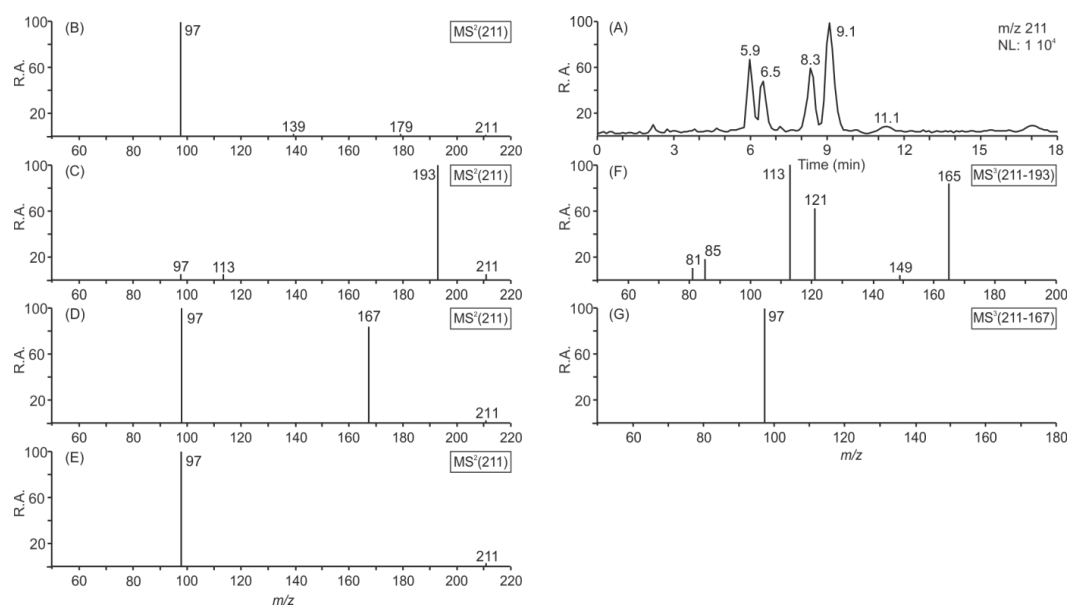
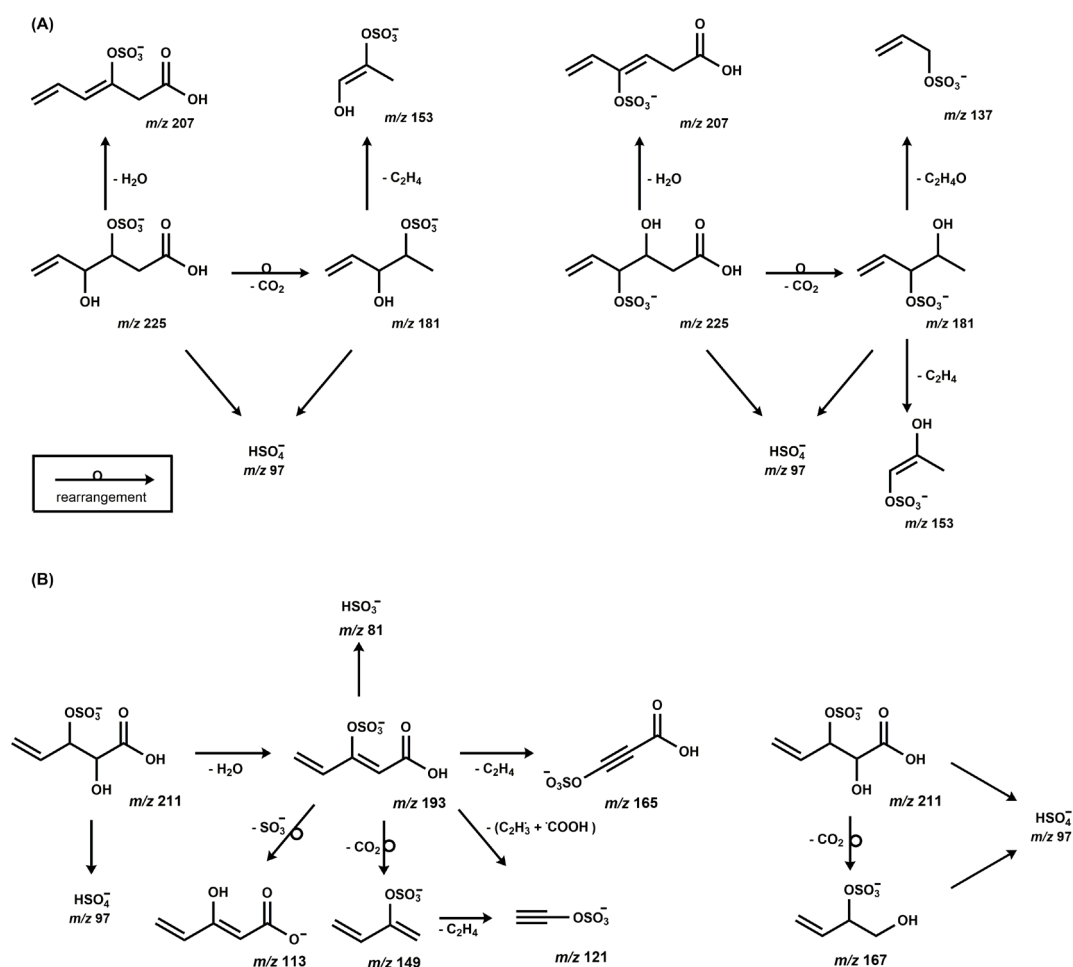


Figure 6.4. Selected LC/MS chromatographic data (m/z 211 EIC) obtained with the ion-pairing RP-LC technique for (A) ambient fine aerosol and selected MS data (MS² and MS³ product ion spectra) for peaks eluting at (B) 5.9 min, (C, F) 6.5 min, (D, G) 8.3 min, and (E) 9.1 min.



Scheme 6.1. Proposed fragmentation routes for deprotonated (A) MW 226 compounds, related to 3-*Z*-hexenal SOA, which are assigned to sulfate esters of 3,4-dihydroxyhex-5-enoic acid with the sulfate group at C-3 (left) and C-4 (right) and (B) MW 212 compounds present in ambient aerosol, which are assigned to sulfate esters of 2,3-dihydroxy-4-pentenoic acid with the sulfate group at C-3 (left) and positional isomers with the sulfate group located at C-2 (right).

6.3.2. Structural characterization of MW 212 organosulfates related to (an) unknown BVOC precursor(s)

On the basis of accurate mass measurement of the m/z 211 compounds (RT of 3.5 min) in K-pusztta fine aerosol ($C_5H_7O_7S$; measured mass, 210.99252; error, +0.7 mDa), it can be concluded that these compounds are lower homologs of the 3-Z-hexenal SOA-related MW 226 OSs ($C_6H_9O_7S$). As seen in Figure 6.4(A), four fully resolved peaks with comparable signal intensity could be obtained for ambient fine aerosol with the IP RP-LC technique. However, none of these peaks were found to correspond to m/z 211 compounds present in 3-Z-hexenal SOA. Hence, the MW 212 compounds from ambient fine aerosol do not originate from 3-Z-hexenal SOA. Here, we only discuss the data for the ambient fine aerosol and show that one of the MW 212 compounds is structurally related to the 3-Z-hexenal SOA-derived MW 226 OSs. The presence of the bisulfate (HSO_4^-) ion (m/z 97) in the m/z 211 MS^2 spectra for the four compounds (panels B–E of Fig. 6.4) is in agreement with organosulfates; in addition, the m/z 211 MS^2 spectrum for the second eluting isomer [Figure 6.4(C)] shows an ion at m/z 113, because of the combined loss of water (m/z 193) and SO_3 (80 u), of which the latter supports an organosulfate.^{6,23,30,31}

Detailed interpretation of the MS data (panels C and F of Fig. 6.4) allowed the assignment of the second eluting MW 212 compound to a sulfate ester of 2,3-dihydroxy-4-pentenoic acid with the sulfate group located at C-3 [Scheme 6.1(B)]. A minor corresponding diastereoisomer with a similar fragmentation pattern was present at RT of 11.1 min.

The third eluting MW 212 compound (RT of 8.3 min) only showed limited fragmentation through the loss of CO_2 (m/z 167) and formation of m/z 97 (panels D and G of Figure 6.4); hence, its attribution to a positional isomer, i.e., a sulfate

ester of 2,3-dihydroxy-4-pentenoic acid, with the sulfate group located at C-2 should be regarded as tentative (right of Scheme 6.1B).

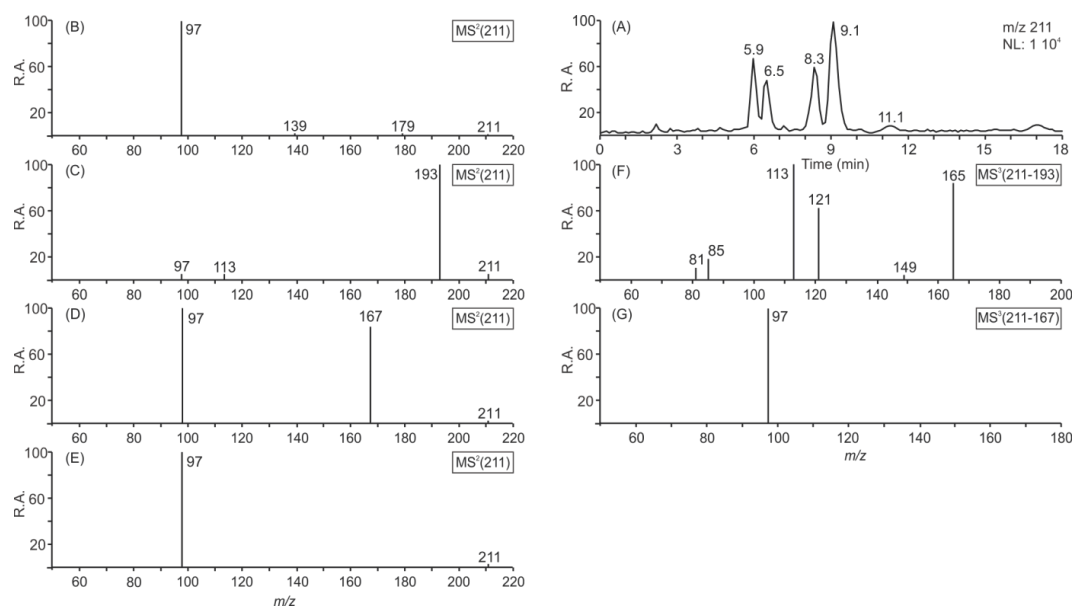


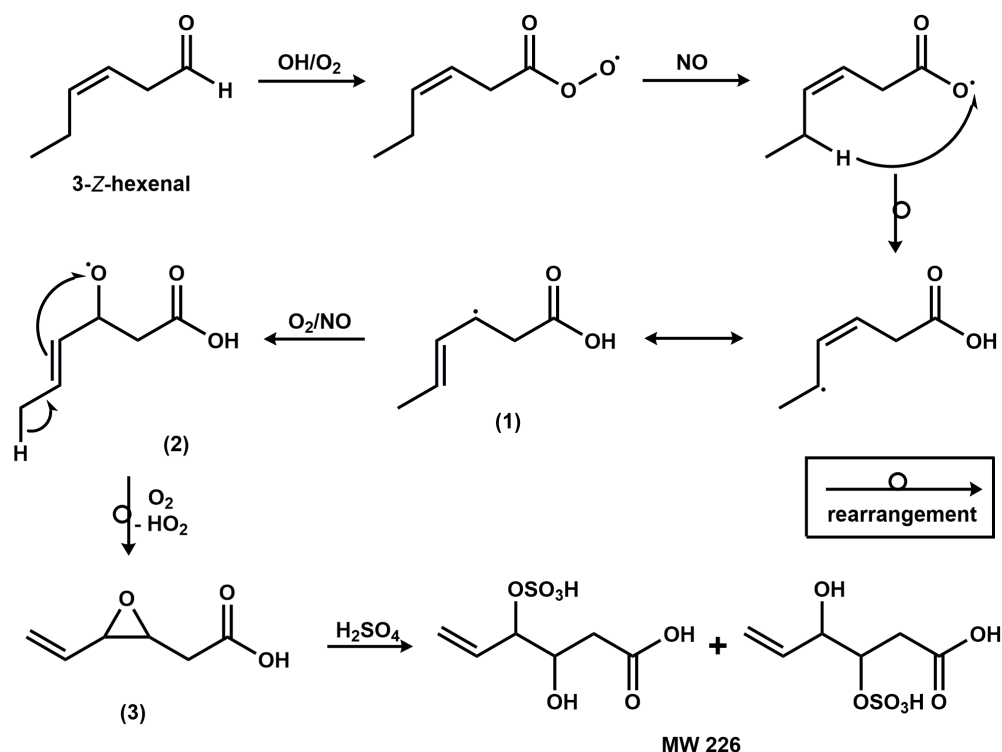
Figure 6.4. Selected LC/MS chromatographic data (m/z 211 EIC) obtained with the ion-pairing RP-LC technique for (A) ambient fine aerosol and selected MS data (MS^2 and MS^3 product ion spectra) for peaks eluting at (B) 5.9 min, (C and F) 6.5 min, (D and G) 8.3 min, and (E) 9.1 min.

6.3.3. Formation pathways for the organosulfates related to 3-*Z*-hexenal SOA

The MW 226 compounds could be assigned to OSs of 3,4-dihydroxyhex-5-enoic acid with the sulfate group positioned at C-3 or C-4. A possible formation pathway leading to these isomeric organosulfates is presented in Scheme 6.2. The proposed pathway involves the formation of a radical species with the radical located at the C-3 position (species 1), followed by reaction with oxygen and NO, resulting in a C₆ alkoxy radical (species 2). The latter species may undergo a rearrangement, resulting in an unsaturated C₆-epoxy carboxylic acid (3). Subsequent sulfation of the epoxy group in the particle phase leads to isomeric

organosulfates of 3,4-dihydroxyhex-5-enoic acid with the sulfate group positioned at C-3 or C-4. The formation of the intermediate radical species (1) is proposed to proceed through OH abstraction of the aldehydic hydrogen atom, reaction with oxygen, and an intramolecular hydrogen rearrangement reaction. With regard to hydrogen abstraction from the aldehydic group, it is known that the OH reaction with 2-*E*-hexenal leads to both OH addition to the double bond and hydrogen abstraction from the aldehydic group;¹¹ however, such data are not available for 3-*Z*-hexenal.

An alternative mechanistic route leading to the formation of OSs from 3-*Z*-hexenal that was considered and does not require epoxide formation is reactive uptake in the particle phase, followed by reaction with the sulfate radical anion.^{19,20} This pathway was proposed for the formation of OSs from the isoprene gas-phase oxidation products methacrolein and methyl vinyl ketone.²⁰⁻²² However, it results in saturated OSs and, thus, does not allow to explain the formation of the unsaturated OSs found for 3-*Z*-hexenal in the current study.



Scheme 6.2. Proposed formation pathway for the MW 226 organosulfates related to 3-Z-hexenal SOA, assigned to sulfate esters of 3,4-dihydroxyhex-5-enoic acid.

6.4. Atmospheric implications

In the present study, we have demonstrated that the plant volatile 3-Z-hexenal serves as a precursor for polar organosulfates with MW 226, which occur in ambient fine aerosol at concentrations comparable to those of the isoprene SOA-related 2-methyltetrol OSs. The source of the MW 212 OSs, which have a substantial abundance in ambient fine aerosol and comprise one isomer that is structurally related to the MW 226 OSs, remains to be established but is likely a plant volatile related to 3-Z-hexenal.

The formation of the MW 226 OSs from 3-Z-hexenal is tentatively explained through a rearrangement of an alkoxy radical into an epoxy carboxylic acid in the gas phase and subsequent sulfation of the epoxy group with sulfuric acid in the

particle phase. Further research is warranted to explore this novel SOA formation pathway for BVOCs. The formation of OSs through epoxy intermediates is in line with a previously suggested pathway for the formation of OSs that are related to isoprene (i.e., the 2-methyltetrols¹⁵ and 2-methylglyceric acid¹⁷), β -pinene (i.e., β -pinanediol³²), and 2-methyl-3-buten-2-ol (i.e., 2,3-dihydroxyisopentanol³³). We speculate that, in addition to 3-Z-hexenal, other plant and floral volatiles serve as precursors for polar organosulfates. In this context, it would be worthwhile to examine commonly occurring green leaf and floral volatiles as biogenic sources for polar organosulfates that are present in ambient fine aerosol and have not yet been elucidated.

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CHAPTER 7

Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes 2-*E*-pentenal, 2-*E*-hexenal, and 3-*Z*-hexenal

Adapted from:

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7.1 Introduction

Volatile organic compounds are ubiquitous in the troposphere, playing a key role as precursors for ozone and SOA. The formation and aging of SOA has received considerable attention during the last two decades because of its potential impact on climate and human health. Major classes of SOA precursors studied include alkanes, alkenes, aromatic hydrocarbons and oxygenated compounds, both from anthropogenic and biogenic origin. Among the BVOCs that are precursors for SOA, isoprene and monoterpenes have received ample attention [for a review, see Hallquist et al. (2009)¹], while other reactive VOCs such as green leaf volatiles have been far less examined. However, recent studies demonstrate that GLVs are also potential precursors for biogenic SOA.²⁻⁶

GLVs comprise unsaturated C₆ compounds that are released by plants when they are wounded (e.g., grass cutting, animal grazing, storms) or attacked by insects. They are named after their specific “green” odor, the fresh scent emitted by green plants, and play a crucial role in plant-plant and plant-insect communication.⁷⁻⁹

GLVs are formed in plant leaves from the unsaturated fatty acids linoleic and α -linolenic acid, which are essential constituents of cell membrane lipids, by biochemical conversion with the enzymes lipoxygenase and hydroperoxide lyase.⁹ One of the most abundant GLVs, 3-Z-hexenal, is formed by the cleavage of α -linolenic acid, and it partly isomerizes to 2-E-hexenal. Both alkenals can be further metabolized by an alcohol dehydrogenase and alcohol acyltransferase¹⁰ to the corresponding alcohols and their esters.¹¹

GLVs also have a potential role in tropospheric chemistry as they may serve as precursors for ozone and SOA.¹²⁻¹⁴ Recently, the GLVs, 3-Z-hexen-1-ol and 3-Z-hexenyl acetate, and methyl salicylate, methyl jasmonate and 2-methyl-3-butene-2-ol have also been shown to undergo aqueous-phase oxidation with the hydroxyl radical and to result in considerable SOA yields

ranging from 10 to 88%.⁵ SOA formation through photooxidation and ozonolysis was first studied at the molecular level for the GLVs 3-Z-hexen-1-ol and 3-Z-hexenyl acetate by liquid chromatography combined with positive ion electrospray ionization mass spectrometry using lithium as cationization agent.² This study demonstrated that 3-hydroxypropanal, the primary oxidation product of 3-Z-hexen-1-ol, can hydrate and undergo further reactions with other aldehydes resulting in SOA dominated by higher-MW oligomers, while, in contrast, considerably fewer higher-MW species are detected in SOA produced from 3-Z-hexenylacetate. SOA formation was recently examined from turf grass volatiles,⁴ which comprise 3-Z-hexen-1-ol and 3-Z-hexenyl acetate, with near-infrared laser desorption/ionization aerosol mass spectrometry, and the ozonolysis SOA profile was found to closely resemble that of 3-Z-hexen-1-ol and to be dominated by low-volatility, higher-MW compounds such as oligoesters. In addition, there is recent evidence that 3-Z-hexenal results in polar m/z 225 (MW 226) OSs through photooxidation and/or ozonolysis,⁶ which occur at substantial concentrations in fine ambient aerosol (PM_{2.5}) from a forested site in Belgium.¹⁵ OSs are potential marker compounds for SOA formation occurring under acidic conditions by particle-phase reactions with sulfuric acid,¹⁶ formed by oxidation of sulfur dioxide, which is mainly from anthropogenic origin in continental regions of the globe.¹⁷ In addition to formation through reaction with sulfuric acid of epoxy-containing SOA compounds from the oxidation of β -pinene,¹⁸ isoprene^{19,20} and 2-methyl-3-buten-2-ol,²¹ OSs may also result from the reactive uptake of unsaturated compounds in the particle phase and reaction with the sulfate anion radical.²²⁻²⁶ In addition, OSs may also be formed by uptake of tertiary organonitrates in the particle phase and nucleophilic substitution of the nitrate by a sulfate group, as shown in the case of 2-methyltetrol sulfates.^{27,28}

Organosulfates are ubiquitous compounds in our environment, not only formed from BVOCs but also from anthropogenic VOCs such as aromatics.^{29,30} It has been suggested that they are a significant component of fine ambient aerosol.³¹⁻³⁴ Using Fourier transform infrared measurements it was determined that $4 \pm 8\%$ of the organic mass of continental outflow aerosols over the southeast Pacific Ocean during the VOCALS–Rex 2008 campaign was due to organosulfates during periods of high organic and sulfate concentrations.³³ The annual average contribution of organosulfates to organic mass for twelve sites in the United States was found to be 5-10% using a S-estimation method, and was higher during warm months when photochemical oxidation chemistry is most active.³⁴ As to K-puszt, Hungary, it was shown that organosulfates correspond to a substantial fraction of fine ambient summer aerosol, which was determined with S-estimation methods to be as high as 30% of the total organic mass³¹ and to correspond to 6-12% of the bulk sulfur mass.³²

The present study focuses on the chemical characterization of m/z 169, 213 and 229 OSs formed from the C_5 -unsaturated aldehyde, 2-*E*-pentenal, which is a known photolysis product of 3-*Z*-hexenal,³⁵ as well as from the C_6 -unsaturated aldehydes 2-*E*-hexenal and 3-*Z*-hexenal. In a previous study,³⁶ it was shown that fine ambient aerosol ($PM_{2.5}$) contains polar m/z 213 OSs (i.e., sulfate esters of 2,3-dihydroxypentanoic acid), which could be related to 2-*E*-pentenal, have the same magnitude as the m/z 215 OSs that originate from isoprene^{31,37} and are formed through sulfation of intermediary C_5 -epoxydiols.^{19,38} Formation pathways for the m/z 213 and 229 OSs that originate from 2-*E*-pentenal are proposed, thereby considering a known route leading to OSs, namely, the route established for 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein in the presence of NO_x , which, as 2-*E*-pentenal, is also an α,β -unsaturated aldehyde.²⁰

A first step in understanding the impact of an unknown organosulfate (or any organic compound) in the environment is its characterization at the molecular level, as this knowledge allows one to obtain information on its VOC precursor and its formation process (for a review, see Nozière et al., 2015).³⁹ Only after its molecular structure has been established, ambient monitoring studies can be considered involving quantitative measurements, which allow one to obtain further insights into its formation.

In order to chemically characterize the unknown OSs from 2-*E*-pentenal in detail laboratory smog chamber experiments were conducted in the present study with 2-*E*-pentenal, 3-*Z*-hexenal and 2-*E*-hexenal, and the organosulfate profiles were compared with those of ambient fine (PM_{2.5}) aerosol collected from K-pusztá, Hungary, a rural site with mixed deciduous-coniferous vegetation. For the chemical analysis, LC/(–)ESI-MS was performed by resorting to RP-LC using a trifunctionally-bonded C₁₈ stationary phase.³⁷ As to mass spectrometric techniques, use was made of high-resolution MS to infer the elemental composition, while ion trap MS was employed to obtain information about functional groups and their position in the molecules, a state-of-the-art analytical methodology which has proven its usefulness in previous studies on the molecular characterization of organosulfates^{6,31,36,37} and SOA (for a review, see Nozière et al., 2015).³⁹ In addition, quantum chemical calculations were performed to gain insight into the distinctive mass spectral behavior of positional isomers containing neighboring sulfate, hydroxyl, and carboxyl groups.

7.2. Experimental section

7.2.1. Chemicals

Methanol (ULC/MS grade) used for sample preparation and as LC mobile phase and acetonitrile (HPLC supra-gradient grade) were from Biosolve NV (Valkenswaard, The Netherlands); and *cis*-pinonic acid (purity: 98%; for MS

signal optimization) was from Sigma-Aldrich (St. Louis, MI, USA). High-purity water (18.2 MΩ •cm; total organic carbon, 2 ppb) used for redissolving aerosol extracts and preparing the aqueous LC mobile phase was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). 2-*E*-pental (purity: 95%), 2-*E*-hexenal (purity: 98%) and 3-*Z*-hexenal (50% solution in triacetin) used for smog chamber experiments and 2-*E*-pentenoic acid (purity: 98%) used for the dark aqueous phase experiments with the sulfate anion radical were from Sigma-Aldrich.

7.2.2. Aerosol samples

7.2.2.1. Laboratory SOA samples

Table 7.1 summarizes the experimental conditions for the selected biogenic VOC (i.e., 2-*E*-pental, 2-*E*-hexenal and 3-*Z*-hexenal) chamber experiments used in the present study. For details about the experimental conditions, see Chapter 3, Section 3.3. For details about the sample preparation, see Chapter 3, Section 3.4.

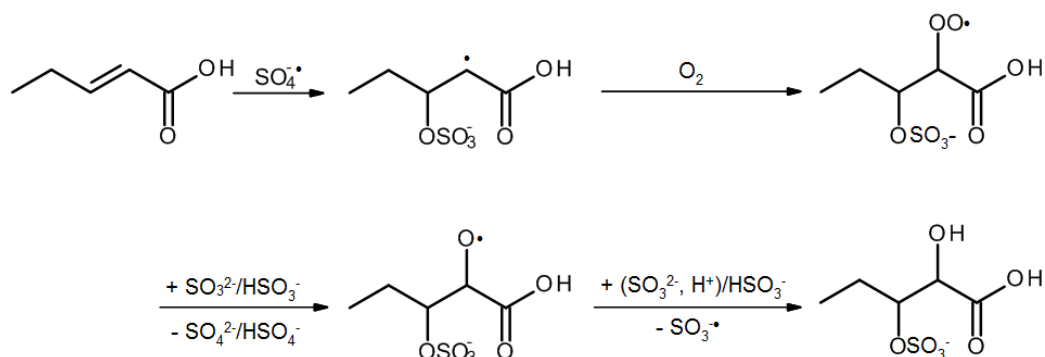
7.2.2.2. Aqueous-phase reaction products

Aqueous-phase reaction products of 2-*E*-pentenoic acid, containing 3-sulfooxy-2-hydroxypentanoic acid, were obtained following the method reported by Ziajka and Rudzinski (2007) with adaptations.⁴⁰ The formation of organosulfates is based on attack of the double bond with the sulfate radical anion [e.g., Rudzinski et al., (2009)²²]; the reaction is shown in Scheme 7.1. A round-bottom flask of 50 mL volume was filled with 30 mL of an aqueous solution that contained dissolved atmospheric oxygen, sodium sulfite (SIV) (4.7×10^{-3} M) and 2-*E*-pentenoic acid (9.6×10^{-3} M). The pH of the solution was adjusted to 3.1 with 0.1 M H₂SO₄, and the autoxidation of sulfite by the dissolved atmospheric oxygen was catalyzed by injecting a small aliquot of Fe₂(SO₄)₃ catalyst solution (2.5×10^{-5} M). The experiment was carried out at 25 ± 0.1 °C and the reaction time at which the 2-*E*-pentenoic acid reaction products were sampled was 5 min.

Table 7.1. Experimental chamber conditions for experiments used for the structural characterization of unknown organosulfates related to 2-*E*-pentenal, 2-*E*-hexenal and 3-*E*-hexenal SOA.

Sample code		ER625–GF5	ER627 – GF10	ER684–GF5
Hydrocarbon		2- <i>E</i> -pentenal	3- <i>Z</i> - hexenal	2- <i>E</i> -hexenal
Hydrocarbon Conc.	Initial:	4.8 ppmC	2.5 ppmC	11.3 ppmC
	Steady State:	1.1 ppmC	0.3 ppmC	4.3 ppmC
NO_x * Conc.	Initial:	280 ppb	290 ppb	400 ppb
	Steady State:	178 ppb	200 ppb	195 ppb
O₃ Conc.	Initial:	-	-	-
	Steady State:	207 ppb	280 ppb	207 ppb
OC Conc.	Initial:	-	-	-
	Steady State:	4.9 µg m ⁻³	5 µg m ⁻³	20.1 µg m ⁻³
Seed type		½ AS + ½ SA	½ AS + ½ SA	½ AS + ½ SA
Conc.		28 µg m ⁻³	30 µg m ⁻³	26 µg m ⁻³
Other Conditions		4 light banks 516 nmol m ⁻³ [H ⁺] air, RH: 28%	4 light banks 439 nmol m ⁻³ [H ⁺] air RH: 29%	4 light banks 587 nmol m ⁻³ [H ⁺] air RH: 29%

*All the initial NO_x was NO.



Scheme 7.1. Formation mechanism for the sulfate ester of 2,3-dihydroxypentanoic acid with the sulfate group located at C-3 through reaction of 2-*E*-pentenoic acid with the sulfate radical anion in aqueous solution.

7.2.2.3. Ambient fine aerosol

See Chapter 3, Sections 3.2 and 3.4.

7.2.3. Liquid chromatography/mass spectrometry

7.2.3.1. Liquid chromatography

Use was made of regular RP-LC with an Atlantis T3 column. See Chapter 3, Section 3.6.3 for further details.

7.2.3.2. Mass spectrometry

A linear ion trap mass spectrometer (LXQ, Thermo Scientific) was used in this work, for the operation conditions, see Chapter 3, Section 3.6.3.

Accurate mass measurements were carried out using a Synapt G2-S HDMS instrument (Waters) equipped with an electrospray ion source and quadrupole – time-of-flight type mass analyzer. The instrument was controlled and recorded data were processed using MassLynx V4.1 software (Waters). The chromatographic separation was performed with ultra-performance LC (UPLC) using a HSS T3 column (2.1 x 100 mm; 1.8 μ m particle size; Waters), which as the Atlantis T3 column (Waters) contains a stationary phase based on trifunctionally-bonded C₁₈ chains. The measurements were only carried out for

the ambient K-pusztta PM_{2.5} aerosol extract and were mainly performed to obtain accurate mass data on the deprotonated molecules and their MS² product ions.

7.2.4. Quantum chemical calculations

Calculations on isomeric 2,3-dihydroxypentanoic acid sulfates were performed using the Gaussian09 suite of programs^{41,42} applying density functional theory (DFT) with the B3LYP functional⁴² and the 6-311 G basis set, as it is implemented in Gaussian09. Geometry optimizations were performed for the isolated molecules in the gas phase.

7.3. Results and discussion

7.3.1. Organosulfate profiles in ambient fine aerosol due to SOA from 2-E-pentenal, 3-Z-hexenal, and 2-E-hexenal

Figure 7.1 shows selected LC/MS chromatographic data obtained for K-pusztta fine aerosol, including a BPC and EICs at m/z 215, 229, 213 and 169, corresponding to the deprotonated forms of OSs related to isoprene (m/z 215) and 2-E-pentenal, 3-Z-hexenal, and 2-E-hexenal (m/z 229, 213, and 169). The m/z 229, 213 and 169 compounds will be structurally characterized and discussed in the following sections. The LC/MS chromatographic data reveal that the targeted OSs at m/z 229, 213 and 169 have a substantial relative abundance compared to that of the m/z 215 compounds in ambient fine aerosol, which correspond to isoprene SOA compounds, i.e., sulfate esters of the 2-methyltetrols, formed by sulfation of intermediary C₅-epoxydiols.^{19,38} The structures of the BVOC precursors 2-E-pentenal, 2-E-hexenal and 3-Z-hexenal, and the identified organosulfates with their elemental formula, measured m/z value and m/z values of main product ions are summarized in Table 7.2.

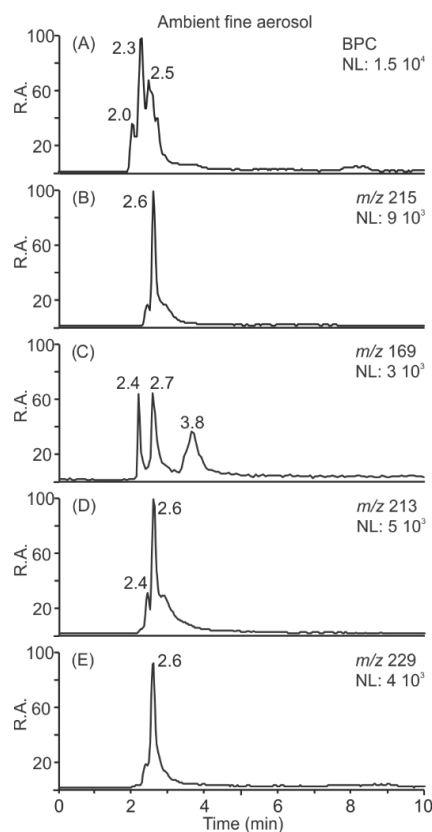
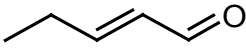
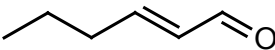
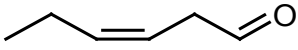
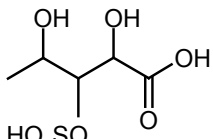
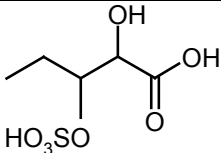
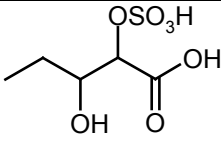
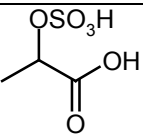
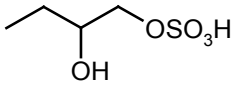


Figure 7.1. Selected LC/MS chromatographic data using regular RP-LC obtained for ambient fine aerosol, including a BPC and EICs at m/z 215, 169, 213 and 229, corresponding to the deprotonated forms of OSs related to isoprene (m/z 215) and OSs related to 2-*E*-pentenal (m/z 229, 213, and 169).

Table 7.2. Chemical structures of 2-*E*-pentenal, 2-*E*-hexenal, and 3-*Z*-hexenal, and of their identified organosulfates with mass spectral data (m/z , elemental formula, and m/z of main product ions).

VOC precursors		
		
2- <i>E</i> -pentenal	2- <i>E</i> -hexenal	3- <i>Z</i> -hexenal
Identified organosulfates	m/z (measured) (formula)	m/z product ions
 3-sulfooxy-2,4-dihydroxy-pentanoic acid	229.0021 (C ₅ H ₉ O ₈ S)	MS ² (229): 211, 195, 149, 97 MS ³ (229-149): 131, 103, 75 MS ³ (229-185): 167, 153, 141, 123 MS ³ (229-211): 193, 181, 167, 139, 97
 3-sulfooxy-2-hydroxy-pentanoic acid	213.0071 (C ₅ H ₉ O ₇ S)	MS ² (213): 195, 133, 97 MS ³ (213-133): 75
 2-sulfooxy-3-hydroxy-pentanoic acid	213.0065 (C ₅ H ₉ O ₇ S)	MS ² (213): 195, 181, 169, 97 MS ³ (213-169): 151, 137, 97 MS ⁴ (213-169-137): 81, 73
 lactic acid sulfate	168.9807 (C ₃ H ₅ O ₆ S)	MS ² (169): 151, 125, 97
 1-sulfooxy-2-hydroxy-butane	169.0177 (C ₄ H ₉ O ₅ S)	MS ² (169): 151, 137, 97 MS ³ (169-137): 81, 73

7.3.2. Structural characterization of m/z 229 organosulfates related to 2-*E*-pentenal

Figure 7.2 (A – F) shows selected LC/MS chromatographic data (m/z 229 EICs) for ambient fine aerosol and SOA generated from 2-*E*-pentenal in the presence of acidic seed aerosol, as well as selected MS data (MS^2 and MS^3 product ion spectra). Selected LC/MS data (m/z 229 EICs and MS^2 spectra) for SOA generated from 2-*E*-hexenal and 3-*Z*-hexenal, showing that m/z 229 compounds are also formed although at a lower relative abundance than for 2-*E*-pentenal SOA, are provided in Figure 7.3. Accurate mass measurement of the m/z 229 OSs present in K-pusztai fine aerosol led to the elemental formula of $C_5H_9O_8S$ (RT 2.5 min: measured mass: 229.0021, error: +0.3 mDa; RT 2.2 min; measured mass: 229.0009, error: –0.9 mDa). Additional MS^3 data obtained for the m/z 229 OSs present in K-pusztai fine aerosol are given in Figure 7.4(A, B). Detailed interpretation of the MS data led to the assignment of the m/z 229 OSs as stereoisomeric forms of a sulfate ester of 2,3,4-trihydroxypentanoic acid, i.e., 3-sulfooxy-2,4-dihydroxypentanoic acid (Table 7.2; Scheme 7.2). The presence in the m/z 229 MS^2 spectra (Fig. 7.2) of the bisulfate [HSO_4^-] ion (m/z 97) as well as the loss of SO_3 (80 u) leading to m/z 149 are consistent with an organosulfate, whereas the losses of H_2O (18 u) and CO_2 (44 u), affording m/z 211 and m/z 185, indicate a hydroxyl and a carboxyl group, respectively.^{6,36,37,43,44} Other diagnostic ions formed upon further fragmentation of m/z 149 include m/z 131 (loss of H_2O), m/z 103 (loss of C_2H_6O), and m/z 75 (loss of $C_3H_6O_2$). The sulfate group is located at the C-3 position based on diagnostic product ions formed by further fragmentation of m/z 185 [Fig. 7.4 (A)] at m/z 167, 153, 141, and 123 (Scheme 7.2). Ions formed by further fragmentation of m/z 211 [Fig. 7.4(B)] to m/z 193, 167 and 97 are also explained in Scheme 7.2.

Furthermore, it is noted that the m/z 229 profiles obtained for K-pusztá fine aerosol and 2-*E*-pentenal (Fig. 7.2) are quite comparable, revealing a major compound eluting at 2.5 min, while additional later-eluting isomers could be observed for 3-*Z*-hexenal and 2-*E*-hexenal SOA (Fig. 7.3). Since only the m/z 229 peak eluting at 2.5 min is found in ambient fine aerosol, no attention is given to the latter later-eluting 3-*Z*-hexenal and 2-*E*-hexenal SOA isomers. As 2,3,4-trihydroxypentanoic acid has three chiral carbon atoms, several stereoisomeric forms (theoretically eight) are indeed possible. An early-eluting m/z 229 isomer (RT 2.2 min) is detected in fine ambient aerosol that is not formed from 2-*E*-pentenal, 3-*Z*-hexenal, and 2-*E*-hexenal. Selected MS data for the latter isomer are provided in Figure 7.5. It can be seen that the MS data only differ from those of the major peak at RT 2.5 min by the relative abundances of the product ions, consistent with stereoisomers.

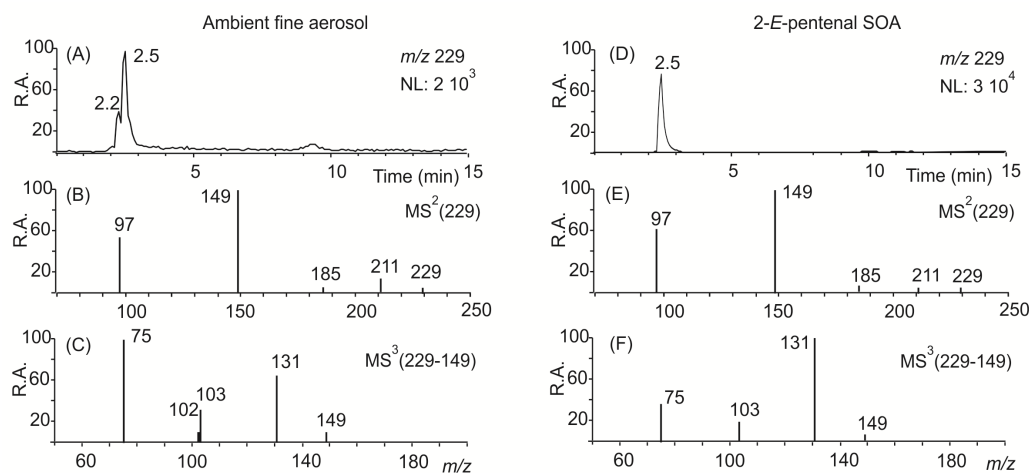


Figure 7.2. Selected LC/MS chromatographic data (m/z 229 EICs) for (A) ambient fine aerosol and (D) SOA generated from 2-*E*-pentenal in the presence of acidic seed aerosol, as well as selected MS data (MS^2 or MS^3 product ion spectra) for the peak eluting at 2.5 min in (B, C) ambient aerosol and (E, F) 2-*E*-pentenal SOA.

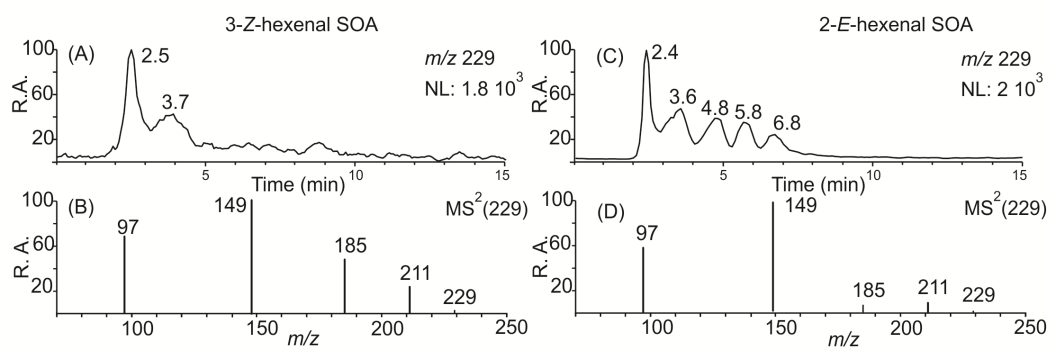


Figure 7.3. Selected LC/MS extracted ion chromatographic data (m/z 229) for the selected filters containing 3-Z-hexenal and 2-E-hexenal SOA, as well as a MS^2 product ion spectrum for the peak eluting at 2.5 min and 2.4 min, respectively.

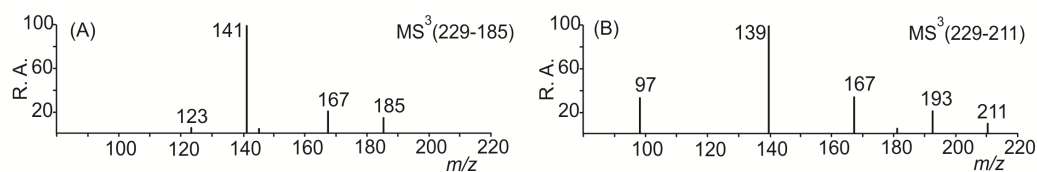


Figure 7.4. Additional MS^3 product ion data for the peak at 2.5 min present in ambient fine aerosol [Fig. 7.2(A)].

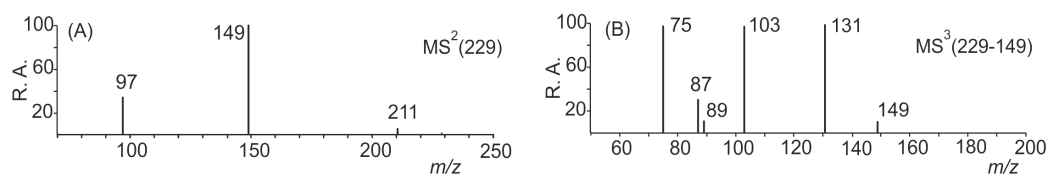
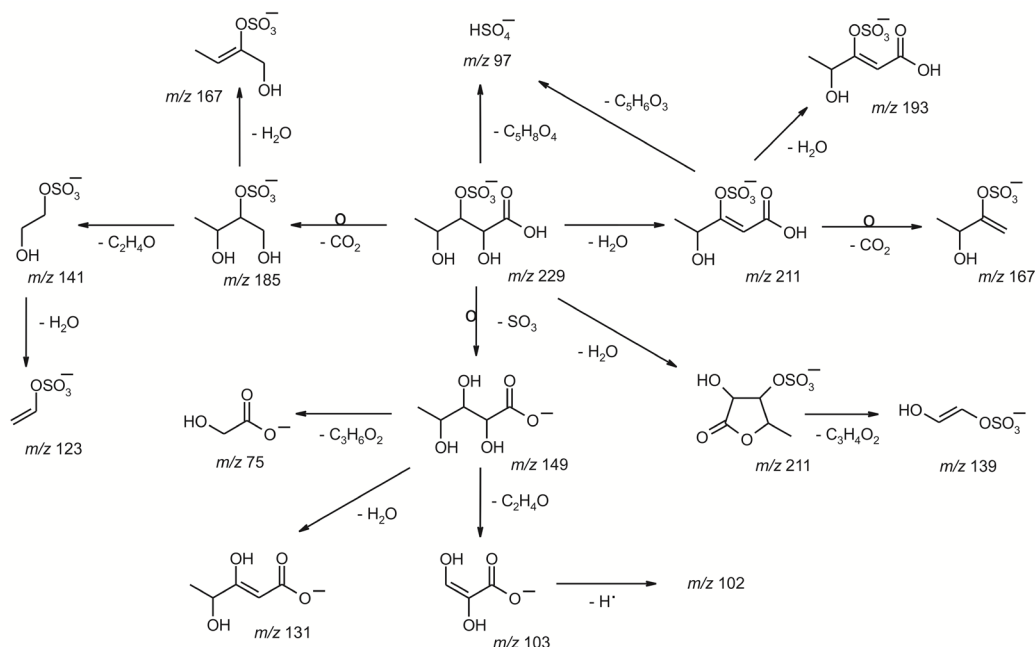


Figure 7.5. Selected MS data (MS^2 or MS^3 product ion spectra) for the peak eluting at 2.2 min in ambient aerosol [Fig. 7.2 (A)].



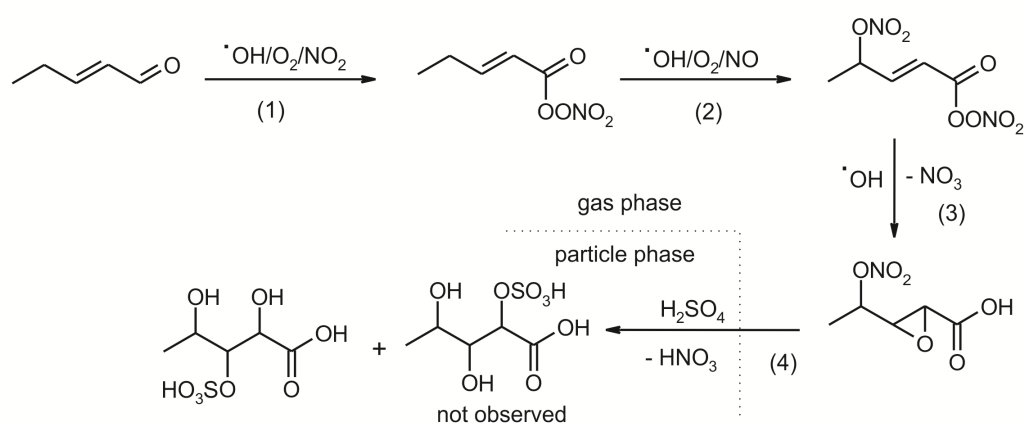
Scheme 7.2. Proposed fragmentation routes for the m/z 229 organosulfate, related to 2-*E*-pentenal SOA and assigned to 3-sulfooxy-2,4-dihydroxypentanoic acid, on the basis of detailed interpretation of MS^2 , MS^3 , and accurate mass data.

7.3.3. Proposed formation pathway for m/z 229 organosulfates formed from 2-*E*-pentenal

As discussed above, m/z 229 compounds detected in 2-*E*-pentenal SOA could be assigned to stereoisomeric forms of 3-sulfooxy-2,4-dihydroxypentanoic acid. The detection of these compounds in 3-*Z*-hexenal SOA is in line with the fact that 2-*E*-pentenal is a photolysis product of 3-*Z*-hexenal.³⁵ The formation of 2-*E*-pentenal through photolysis of 2-*E*-hexenal has not been reported so far although it is very likely that it may also be formed in this way.

A possible formation pathway leading to the structurally characterized isomeric m/z 229 organosulfates is proposed in Scheme 7.3, which bears features of the pathway proposed for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanic

acid from methacrolein, which, as 2-*E*-pentenal, is also an α,β -unsaturated aldehyde.²⁰ Reactions (1) are inspired by the latter pathway, involving abstraction of the hydrogen atom of the aldehyde group with the OH radical, followed by reaction with molecular oxygen and NO₂, resulting in 2-*E*-pentenoylperoxynitrate. Reactions (2) introduce a nitrate group at the C-4 position, which hydrolyzes in the particle phase in the presence of sulfuric acid. Peroxyl radicals (RO₂) react with NO to form organic nitrates (or alkoxy radicals) in the presence of NO,⁴⁵ whereas organic nitrates (RONO₂) hydrolyze to form alcohols and nitric acid in aqueous medium.^{46,47} Reactions (3) and (4) are similar to those established for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein,²⁰ involving formation of an epoxy group in the gas phase and reaction of the latter with sulfuric acid in the particle phase. A possible reason for the failure to detect 2-sulfooxy-3,4-dihydroxypentanoic acid is its instability, as has been observed for *m/z* 213 organosulfates (Section 7.3.4).



Scheme 7.3. Proposed formation pathway for *m/z* 229 (MW 230) organosulfates related to 2-*E*-pentenal (and indirectly to 3-*Z*-hexenal and 2-*E*-hexenal SOA), which occur in ambient fine aerosol, and are assigned to 3-sulfooxy-2,4-dihydroxypentanoic acid. The suggested route shares features of the mechanism reported for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein (Lin et al., 2013).²⁰

7.3.4. Structural characterization of m/z 169 and 213 organosulfates related to 2-*E*-pentenal

Figure 7.6 shows selected LC/MS chromatographic data (m/z 213 EICs) for ambient fine aerosol and 2-*E*-pentenal SOA, as well as selected MS data (MS^2 and MS^3 product ion spectra). Analysis of the m/z 213 peaks in ambient fine aerosol (Figure 7.6 A) eluting between 2.4 and 2.7 min shows that different isomers are present. Accurate mass measurement of the m/z 213 OSs present in K-pusztta fine aerosol led to the elemental formula of $C_5H_9O_7S$ [RT 2.4 min (measured mass, 213.0065; error: -0.4 mDa), RT 2.6 min (measured mass: 213.0071; error: $+0.2$ mDa)]. The major peak in fine ambient aerosol at RT 2.6 min could, on the basis of the MS data [Figs. 7.6 (E, F, G)], be assigned to isomeric 4,5-dihydroxypentanoic acid sulfate esters, which have been structurally characterized in previous work and will not be further discussed here as these isomers are not related to 2-*E*-pentenal SOA.³⁶ Two m/z 213 peaks can be distinguished in 2-*E*-pentenal SOA (Fig. 7.6 K) exhibiting distinctly different mass spectra, of which the first peak at 2.4 min [Fig. 7.6 (L, M, N)] is also present in fine ambient aerosol [Fig. 7.6 (B, C, D)]. Analysis of the MS data obtained for fine ambient aerosol shows that the second m/z 213 isomer present in 2-*E*-pentenal SOA [Fig. 7.6 (O, P)] also occurs in fine ambient aerosol [Fig. 7.6 (H, I)], but that there is co-elution with the 4,5-dihydroxypentanoic acid sulfate esters [Fig. 7.6 (E, G)]. Furthermore, it can be seen that the second-eluting m/z 213 isomer present in 2-*E*-pentenal SOA is also formed in aqueous-phase sulfation of 2-*E*-pentenoic acid [Fig. 7.6 (Q, R, S)]. It is noted that the second-eluting m/z 213 isomer in 2-*E*-pentenal SOA (RT 3.7 min), which elutes as a broad peak and differs in retention time from the same m/z 213 isomer (with the same MS characteristics) occurring in fine ambient aerosol (RT 2.7 min) and aqueous-phase 2-*E*-pentenoic acid reaction products (RT 2.5 min). A possible reason for this unusual chromatographic behavior is

injection of the (hydrophobic) SOA sample leading to a change in the LC column characteristics. In addition, it can be seen that the same m/z 213 isomers are detected in 3-*Z*-hexenal and 2-*E*-hexenal SOA (Fig. 7.7).

Based on the detailed interpretation of the MS data (Scheme 7.4), the two m/z 213 isomers related to 2-*E*-pentenal SOA are attributed to 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid for the first- and second-eluting isomers, respectively (Table 7.2). The first isomer mainly fragments through loss of CO₂ (44 u) and further upon MS³ and MS⁴ fragments to m/z 137 and 73. The second isomer fragments through loss of SO₃ (80 u), affording m/z 133, which in turn upon MS³ fragments further to m/z 75 through the loss of propenal (58 u). The distinctly different fragmentation behavior of the two isomers was addressed through quantum chemical calculations. These calculations provide insight why in the case of the isomer with the sulfate group located at C-3 loss of SO₃ is observed, while this fragmentation is absent for the other isomer with the sulfate group located at C-2. It can be seen from the optimized geometries presented in Figure 7.8 that for 3-sulfooxy-2-hydroxypentanoic acid (A) the negative charge, following elimination of SO₃, can be accommodated by the carboxyl group, which is in close proximity to the C-3 oxygen atom (Scheme 7.4), whereas for 2-sulfooxy-3-hydroxypentanoic acid (B) this process is unlikely.

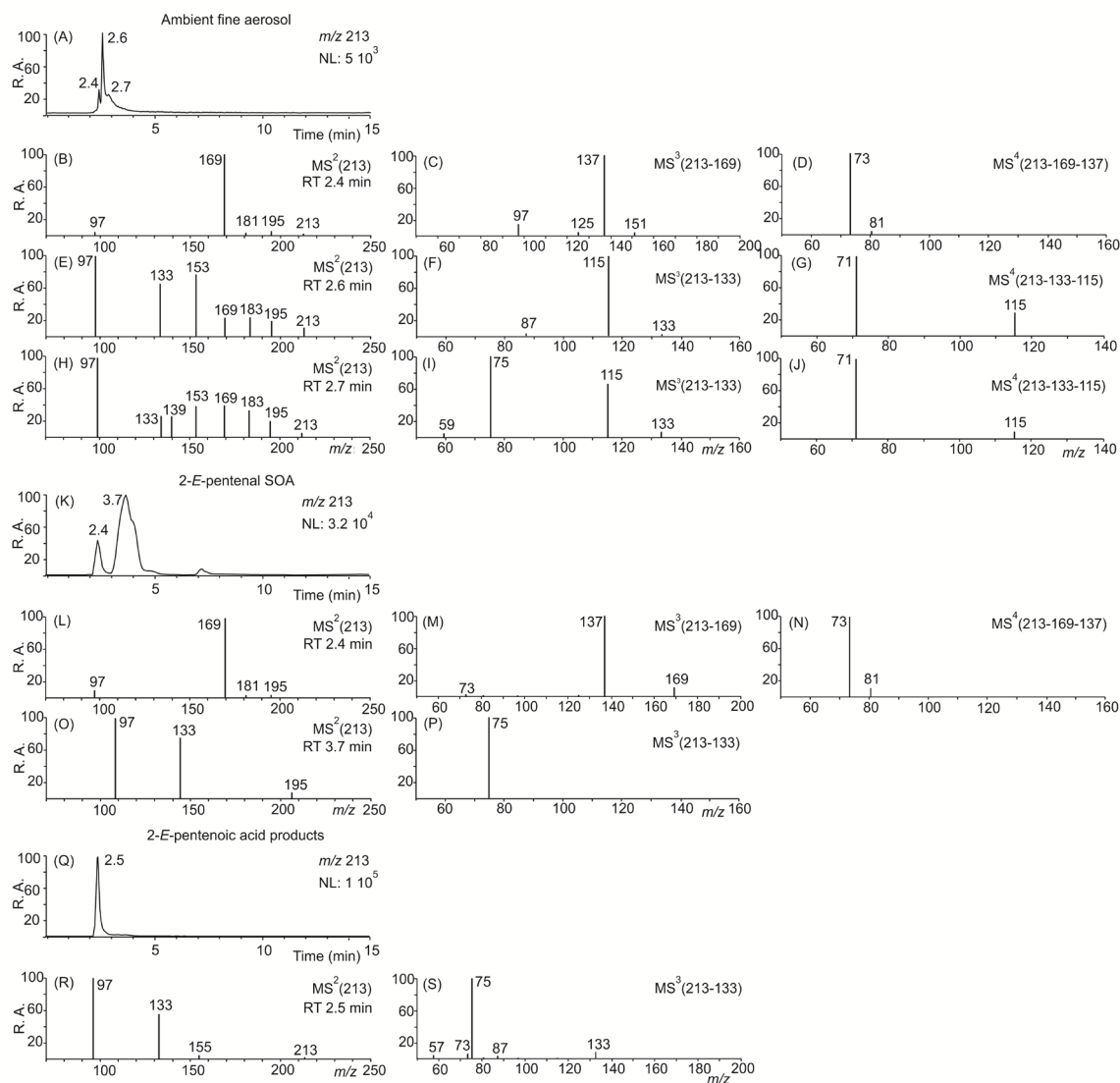


Figure 7.6. Selected LC/MS chromatographic data (m/z 213 EICs) and selected MS data (MS^2 , MS^3 and MS^4 product ion spectra) for ambient fine aerosol (A-J), 2-*E*-pentenal smog chamber SOA (K-P), and 2-*E*-pentenoic acid aqueous-phase SOA (Q-S).

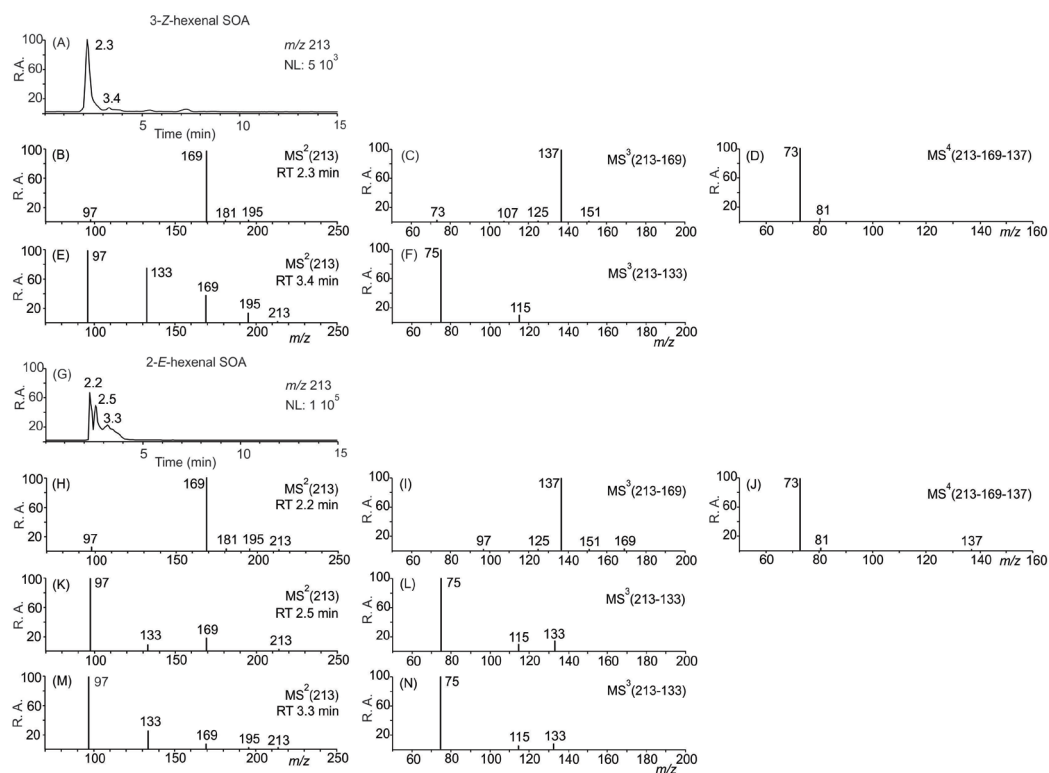
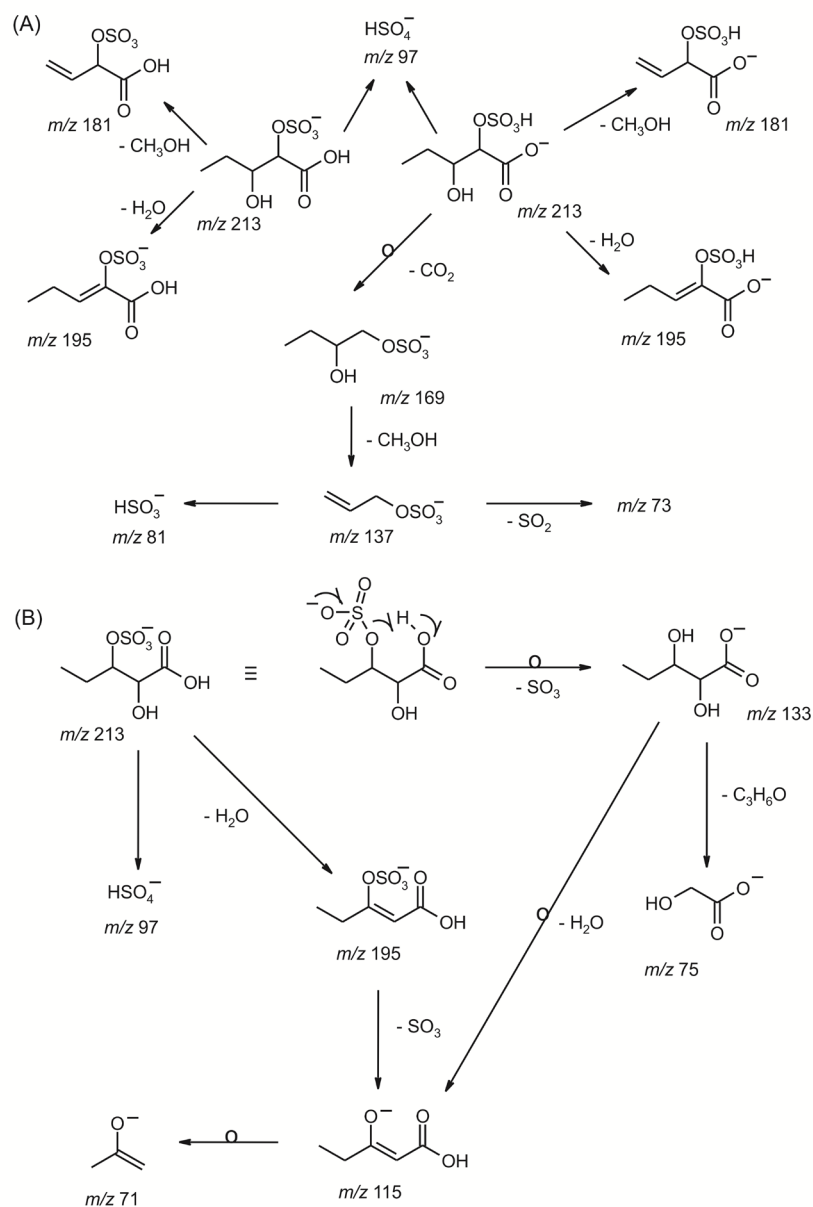


Figure 7.7. Selected LC/MS chromatographic data (m/z 213 EICs) and MS data (MS^2 , MS^3 and MS^4 product ion spectra) for 3-Z-hexenal and 2-E-hexenal SOA.



Scheme 7.4. Proposed fragmentation routes for *m/z* 213 organosulfates, related to 2-*E*-pentenal SOA and assigned to (A) 2-sulfooxy-3-hydroxypentanoic acid and (B) 3-sulfooxy-2-hydroxypentanoic acid, on the basis of detailed interpretation of MS², MS³, MS⁴, and accurate mass data. For the fragmentation of the *m/z* 169 compound, formed by decomposition, see (A).

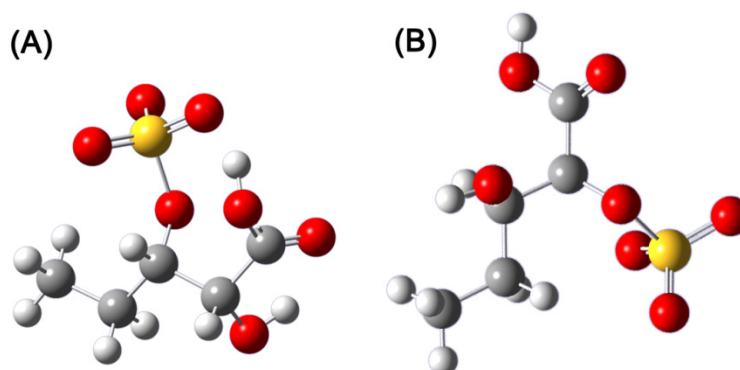


Figure 7.8. Optimized geometries in the gas-phase using ab-initio methods for (A) 3-sulfoxy-2-hydroxypentanoic acid and (B) 2-sulfoxy-3-hydroxypentanoic acid. After loss of SO_3 , the negative charge can be accommodated by the carboxyl group in the case of (A) [see also Scheme 7.4 (B)].

Attention was also given to m/z 169 organosulfates because it was found that they result from the degradation of a m/z 213 OS, as will be discussed in detail below. Figure 7.9 shows selected LC/MS chromatographic data (m/z 169 EICs) obtained for ambient fine aerosol and 2-*E*-pentenal SOA, as well as selected MS data (MS^2 and MS^3 product ion spectra). Three peaks can be distinguished in the m/z 169 EICs, of which the first peak co-elutes with the first-eluting m/z 213 OS (2.4 min), attributed to 2-sulfoxy-3-hydroxypentanoic acid. This co-elution behavior was also noted under improved chromatographic separation conditions where two Atlantis T3 columns were used in series (results not shown). It thus appears that 2-sulfoxy-3-hydroxypentanoic acid is unstable upon electrospray ionization. A possible fragmentation mechanism involving decarboxylation and resulting in m/z 169 is provided in Scheme 7.4(A). The second peak [RT 2.7 min (measured mass, 168.9807; error: -2.9 mDa; elemental formula, $\text{C}_3\text{H}_5\text{O}_6\text{S}$] is attributed to lactic acid sulfate, a known organosulfate, which has been reported in ambient fine aerosol.^{37,48,49} However, since no authentic standard was available, this assignment should be regarded as tentative. The third peak [RT 3.8 min (measured

mass, 169.0177; error: +0.6 mDa; elemental formula, C₄H₉O₅S] reveals a fragmentation pattern that perfectly matches that of the first m/z 169 peak, which is due to decarboxylation. It is thus very likely that this compound results from decarboxylation of the corresponding m/z 213 OS; however, on the basis of this study it could not be determined where the degradation takes place (i.e., on the filter during sampling, during sample workup or during analysis). Furthermore, it was confirmed that the m/z 169 compounds that are present in 2-*E*-pentenal SOA are also formed from 3-*Z*-hexenal and 2-*E*-hexenal (Fig. 7.10). Based on MS data the product with RT 3.8 min in ambient fine aerosol (4.1 min in 2-*E*-pentenal SOA) is assigned to 1-sulfooxy-2-hydroxybutane (Scheme 7.4).

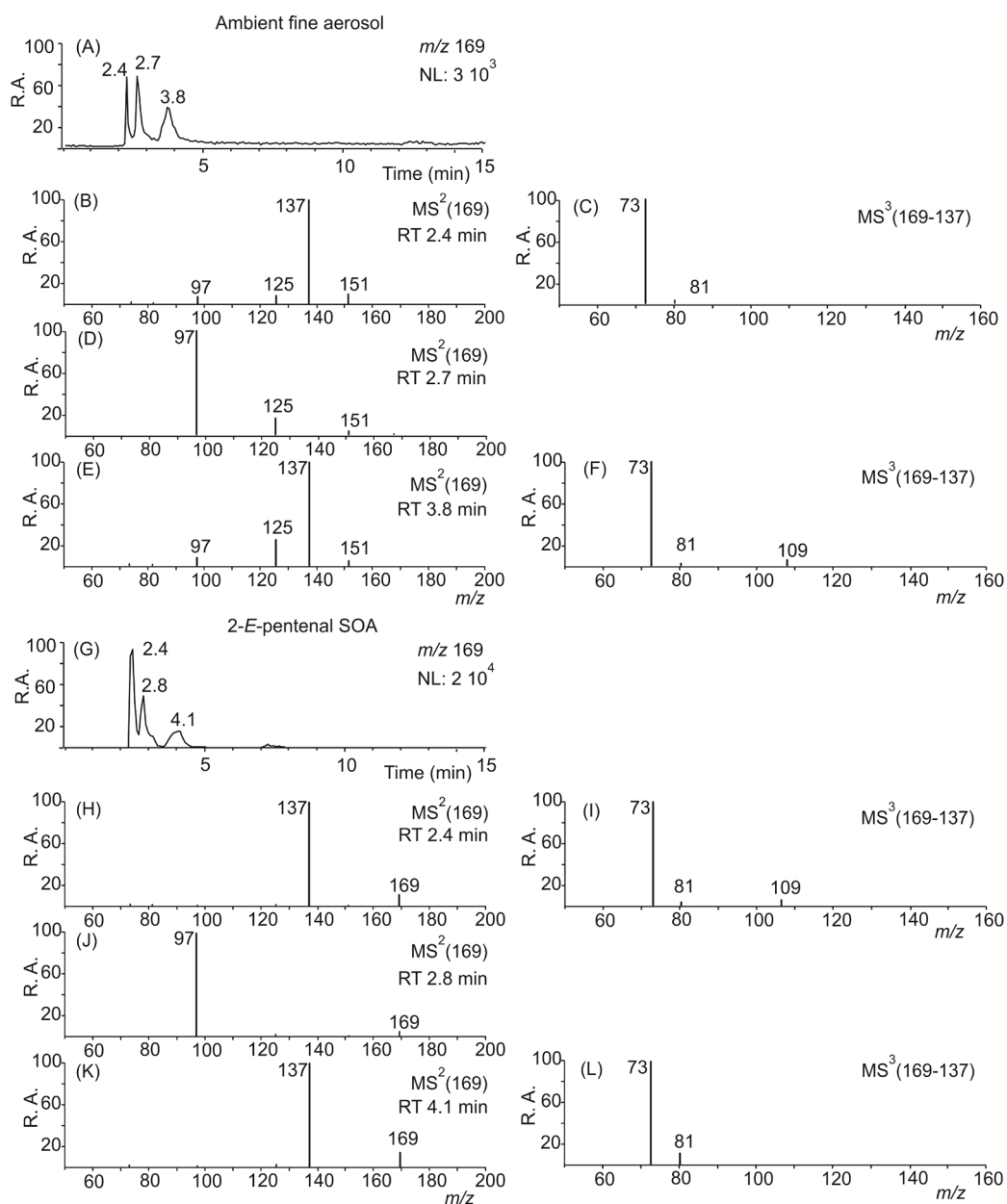


Figure 7.9. Selected LC/MS chromatographic data (m/z 169 EICs) and selected MS data (MS^2 or MS^3 product ion spectra) for ambient fine aerosol (A-F) and 2-E-pentenal SOA (G-L).

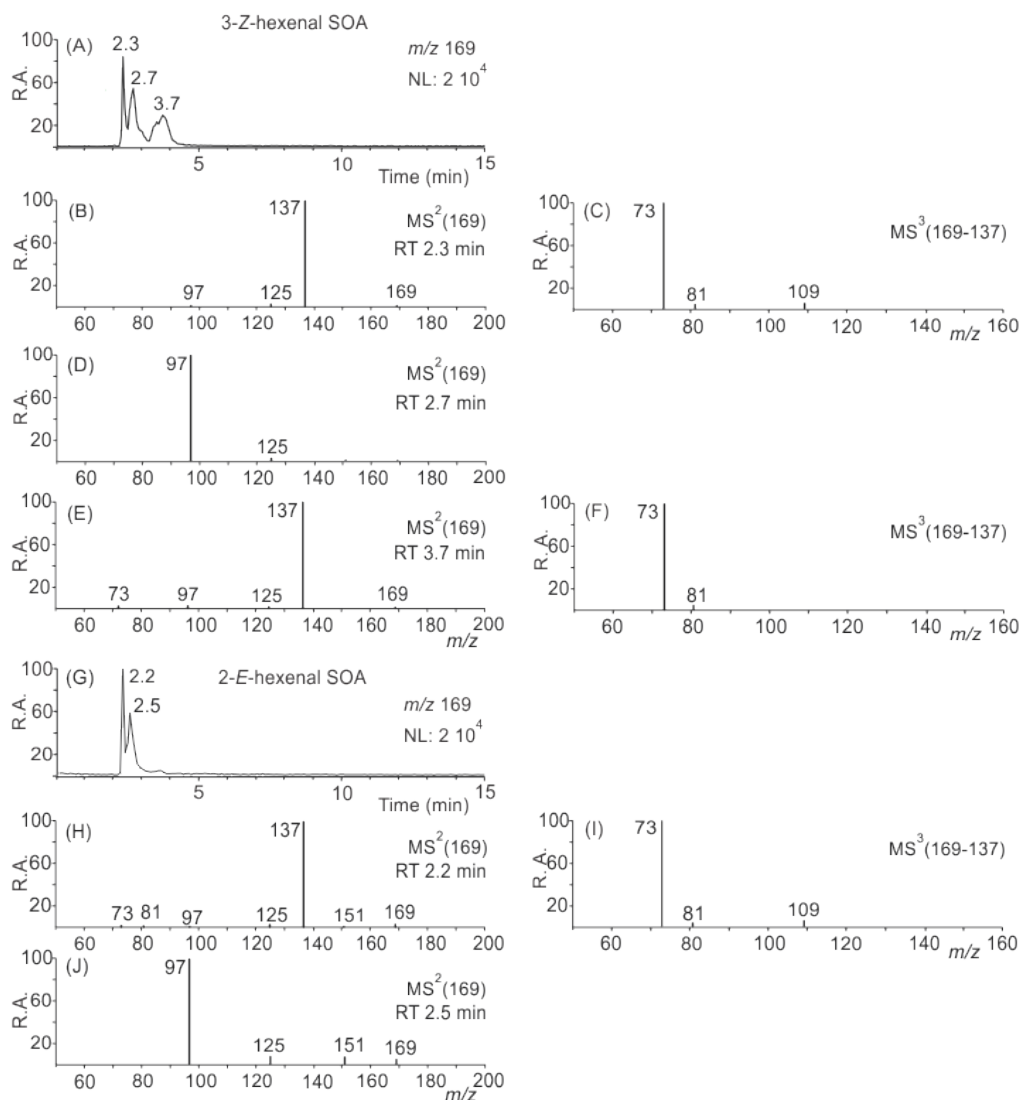
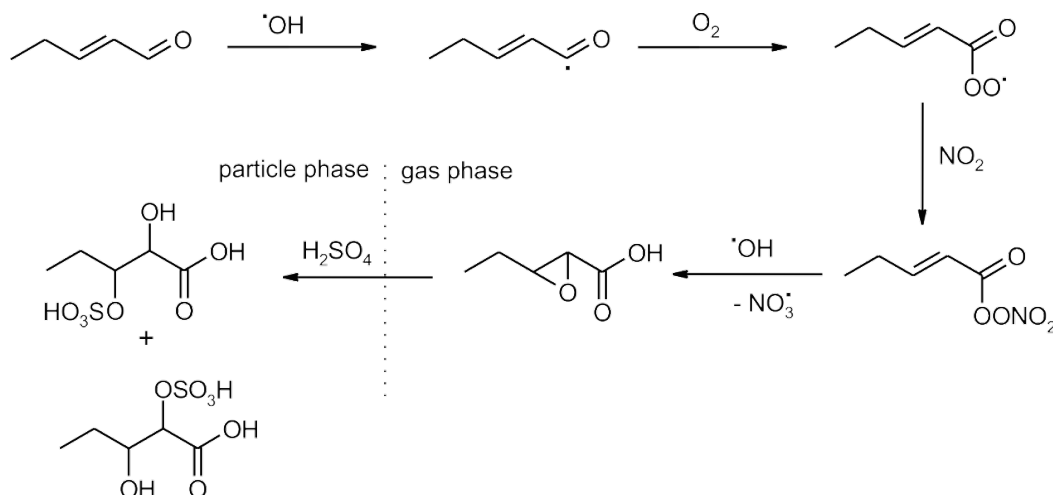


Figure 7.10. Selected LC/MS chromatographic data (m/z 169 EICs) and selected MS data (MS² and MS³ product ion spectra) for 3-*E*-hexenal SOA (A-F), and 2-*E*-hexenal SOA (G-J). The peak at RT 3.7 min in 2-*E*-hexenal SOA is minor, but detailed analysis shows that the same m/z 169 compound as in 3-*Z*-hexenal SOA is present.

7.3.5. Proposed formation pathway for m/z 213 organosulfates formed from 2-*E*-pentenal

As discussed above, m/z 213 compounds detected in 2-*E*-pentenal SOA could be assigned to positional isomeric OSs of 2,3-dihydroxypentanoic acid, i.e., 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid. Their detection in 2-*E*-hexenal and 3-*Z*-hexenal SOA is logical as other organosulfates, i.e., the m/z 229 compounds (Sections 7.3.2 and 7.3.3), could also be found in the latter SOA and the fact that 2-*E*-pentenal is a photolysis product of 3-*Z*-hexenal.³⁵ A possible formation pathway leading to the structurally characterized isomeric m/z 213 organosulfates is proposed in Scheme 7.5. The suggested pathway is based on the mechanism reported for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein, which, as 2-*E*-pentenal, is also an α,β -unsaturated aldehyde.²⁰ It involves a sequence of reactions, comprising epoxidation of the double bond of 2-*E*-pentenal with the OH radical and reaction of the epoxy group with sulfuric acid in the particle phase. The results obtained in this study further suggest that the formation of the m/z 213 sulfate derivatives of 2,3-dihydroxypentanoic acid likely does not result from reactive uptake of 2-*E*-pentenal as only one positional isomer (3-sulfooxy-2-hydroxypentanoic acid) could be generated in the aqueous-phase sulfation of 2-*E*-pentenoic acid, whereas two positional isomers (the latter and 2-sulfooxy-3-hydroxypentanoic acid) are detected in both 2-*E*-pentenal SOA and fine ambient aerosol. The formation of 2-hydroxy-3-sulfooxypentanoic acid in the aqueous-phase reaction of 2-*E*-pentenoic acid with the sulfate radical anion (Scheme 7.1) is caused by stabilization of the resulting intermediate C-2 radical upon attack of the double bond with the sulfate radical anion.



Scheme 7.5. Proposed formation pathway for *m/z* 213 organosulfates related to 2-*E*-pentenal (and indirectly to 3-*Z*-hexenal and 2-*E*-hexenal SOA), which occur in ambient fine aerosol, and are assigned to 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid. The suggested mechanism is based on that reported for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein (Lin et al., 2013).²⁰

7.4. Conclusions and perspectives

We show in the present study that the unsaturated aldehydes, 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal, can be converted into polar organosulfates with *m/z* 229 and 213. These results are in line with a previous study that the green leaf aldehyde 3-*Z*-hexenal serves as a precursor for *m/z* 225 organosulfates.⁶ Thus, in addition to isoprene, the green leaf volatiles, 2-*E*-hexenal and 3-*Z*-hexenal, and 2-*E*-pentenal, a photolysis product of 3-*Z*-hexenal, should be taken into account for organosulfate formation. These results imply that biogenic volatile organic compounds such as the green leaf volatiles, which are emitted due to plant stress (mechanical wounding or insect attack), are a potential source of polar organosulfates and SOA.

Extensive use was made of organic mass spectrometry and detailed interpretation of mass spectral data to elucidate the chemical structures of the m/z 229, 213 and 169 organosulfates formed from 2-*E*-pentenal. In addition, quantum chemical calculations were performed to explain the different mass spectral behavior of 3-sulfooxy-2-hydroxypentanoic acid and 2-sulfooxy-3-hydroxypentanoic acid, where the isomer with the sulfate group at C-3 results in the loss of SO₃. The m/z 213 organosulfates formed from 2-*E*-pentenal are explained by the same route as that reported for 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein, which, as 2-*E*-pentenal, is also an α,β -unsaturated aldehyde. The pathway involves formation of an epoxide in the gas phase and sulfation of the epoxy group with sulfuric acid in the particle phase. The m/z 229 organosulfates formed from 2-*E*-pentenal are tentatively explained by a novel pathway that bears features of the latter pathway but introduces an additional hydroxyl group. Evidence is also presented that the m/z 213 OS, 2-sulfooxy-3-hydroxypentanoic acid, is unstable and decarboxylates, giving rise to 1-sulfooxy-2-hydroxybutane, a m/z 169 organosulfate. The instability of 2-sulfooxy carboxylic acids due to decarboxylation also provides an explanation why in the case of the isoprene-related methacrolein only 3-sulfooxy-2-hydroxy-2-methylpropanoic acid has been detected in previous studies and not its isomer 2-sulfooxy-3-hydroxy-2-methylpropanoic acid. Furthermore, it could be shown that lactic acid sulfate is generated from 2-*E*-pentenal. With regard to the proposed pathways for organosulfate formation from unsaturated aldehydes, further research is warranted to gain additional mechanistic insights.

7.5. References

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Summary and conclusions

Atmospheric aerosols are known to be one of the most important parameters affecting several aspects of our globe, ranging from climate change, air quality, visibility, to human health. In order to predict and understand their role in the chemistry and physics of the atmosphere and our lives, it is necessary to gain insights into their sources, formation mechanisms, properties, and chemical composition. Biogenic volatile organic compounds (BVOCs) are emitted from natural sources (e.g., vegetation) under natural conditions and in response to stress, and are major precursors of atmospheric aerosols, more specifically, of secondary organic aerosol (SOA), that is organic aerosol formed by oxidation of volatile organic compounds, both biogenic and anthropogenic ones, in the gas or particle phase. The focus of this doctoral thesis is on the structural characterization of polar organosulfates, BVOC oxidation products that are of atmospheric interest because they are hydrophilic and as such can affect cloud processes. Organosulfates have a mixed biogenic and anthropogenic origin as they are formed by reaction of BVOCs or their oxidized products with sulfuric acid, which originates from the oxidation of sulfur dioxide, which is mainly from anthropogenic origin. They also contribute to the aerosol acidity because of the presence of the sulfate group. Several mechanisms are known by which organosulfates are formed in the particle phase: (i) reaction of epoxy-containing SOA products (e.g., isoprene-related C₅-epoxydiols) with sulfuric acid; (ii) uptake of unsaturated BVOCs (e.g., methacrolein, a gas-phase oxidation product of isoprene) and reaction with the sulfate radical anion; and (iii) uptake of tertiary organonitrates (e.g., isoprene-related 2-methyltetrol organonitrates) and nucleophilic substitution of the nitrate by the sulfate group. Much information is available about SOA formation from terpenes and isoprene. In contrast, information about SOA formation from green leaf volatiles (GLVs), an important class of BVOCs, which are emitted into the atmosphere when plants are wounded

or attacked by insects, is scarce. 3-*Z*-hexenal is an important GLV formed from the cell membrane unsaturated fatty acid α -linolenic acid by combined reaction of lipoxygenase and hydroperoxide lyase enzymes, and it partly rearranges to 2-*E*-hexenal. The C₅-unsaturated aldehyde 2-*E*-pental is a known photolysis product of 3-*Z*-hexenal.

Two types of aerosol samples were investigated in this work: on the one hand, archived PM_{2.5} aerosol samples that were collected in K-puszt, Hungary, a forested site with a mixed deciduous/coniferous vegetation, during a 2006 summer field campaign, and, on the other hand, SOA samples that were produced from BVOCs serving as precursors for the targeted organosulfates, i.e., the unsaturated aldehydes 2-*E*-pental, 2-*E*-hexenal, and 3-*Z*-hexenal. In addition, reference organosulfates related to the isoprene gas-phase oxidation product methyl vinyl ketone and 2-*E*-pental were prepared by organic synthesis and reaction with the sulfooxy radical anion, respectively. The structural characterization was only performed for those polar organosulfates that are present with a significant relative abundance (relative to that of the isoprene-related C₅-epoxydiol organosulfates) in ambient PM_{2.5} aerosol.

As to analytical methodology, extensive use was made of liquid chromatography in combination with electrospray ionization mass spectrometry in the negative ion mode [LC/(–)ESI-MS], involving ion trap tandem MS, high-resolution MS, and detailed interpretation of the MS data. For the chromatographic separation of the polar organosulfates, LC using a reversed-phase C₁₈ column with polar retention was performed, as well as ion-pairing LC on a reversed-phase C₁₈ column with dibutylammonium acetate (DBAA) as ion-pairing reagent. In selected cases, quantum chemical calculations were performed to gain insight into the MS behavior of organosulfates.

This thesis contains three introductory chapters and four chapters on specific studies, the first three studies corresponding to published papers and the last one corresponding to a manuscript that is in press. The introductory chapters (Chapters 1, 2, and 3) deal with atmospheric aerosols in general, objectives of the research carried out within the frame of this thesis and background on organosulfates, and instrumentation and methods. The four chapters concerning specific studies (Chapters 4, 5, 6, and 7) discuss the structural characterization of novel polar organosulfates that are related to isoprene and the unsaturated aldehydes 2-*E*-hexenal, 3-*Z*-hexenal and 2-*E*-pentenal, as well as the development of an ion-pairing LC method for polar organosulfates.

Chapter 4 deals with the structural characterization of an isoprene-related polar organosulfate with molecular weight (MW) 184 and the structural revision of isoprene-related polar organosulfates with MWs 156, 170, and 200. A considerable fraction of atmospheric particulate fine matter consists of organosulfates, with some of the most polar ones originating from the oxidation of isoprene. The structures of unknown polar organosulfates present in ambient PM_{2.5} aerosol were characterized using LC/(-)ESI-MS, including ion trap MSⁿ and accurate mass measurements, derivatization of the carbonyl group into 2,4-dinitrophenylhydrazones, and in the case of the MW 184 organosulfate, comparison of its LC and MS behaviors with those of synthesized reference compounds. Polar organosulfates with MWs of 156, 170, 184 and 200 were attributed to/or confirmed as sulfate esters of glycolic acid (156), lactic acid (170), 1,2-dihydroxy-3-butanone (184), glycolic acid glycolate (200), 2-methylglyceric acid (200), and 2,3-dihydroxybutanoic acid (200). A more complete structural characterization of polar organosulfates that originate from isoprene SOA was achieved. An important atmospheric finding is the presence of an organosulfate

(MW 184) that is related to methyl vinyl ketone, a major gas-phase oxidation product of isoprene.

Chapter 5 deals with the development of an ion-pairing method for polar isoprene-related organosulfates based on LC/(–)ESI-MS employing a reversed-phase C₁₈ column and DBAA as ion-pairing reagent. Compared to previous work in which use was made of a reversed-phase C₁₈ column with polar retention, an improved separation could be achieved for the isoprene-related polar organosulfates, such as the 2-methyltetrol and 2-methylglyceric acid sulfates, and, hence, their more detailed structural characterization. The best results were obtained with the ion-pairing reagent being present in both the mobile phase and the reconstitution solution, whereby the molar excess of DBAA for the test compounds (methanesulfonate, ethanesulfate, 2-propanesulfate, and D-galactose- 6-sulfate) was more than 103.

Chapter 6 concerns the structural characterization of MW 226 and 212 organosulfates (OSs), which are present at a significant relative abundance in ambient PM_{2.5} aerosol relative to those of the isoprene-related MW 216 organosulfates. Evidence is provided that the GLV 3-*Z*-hexenal serves as a precursor for biogenic SOA through formation of polar MW 226 organosulfates. The MW 226 C₆-OSs were chemically elucidated, along with structurally similar MW 212 C₅-OSs, whose biogenic precursor is likely related to 3-*Z*-hexenal but still remains unknown. Using detailed interpretation of MS data, the MW 226 compounds were assigned to isomeric sulfate esters of 3,4-dihydroxyhex-5-enoic acid with the sulfate group located at the C-3 or C-4 position (i.e., 3-sulfooxy-4-hydroxyhex-5-enoic acid and 4-sulfooxy-3-hydroxyhex-5-enoic acid). Two MW 212 compounds present in ambient fine aerosol were attributed to isomeric sulfate esters of 2,3-dihydroxypent-4-enoic acid, of which two are sulfated at C-3 and one at C-2. The

formation of the MW 226 OSs is tentatively explained through photooxidation of 3-*Z*-hexenal in the gas phase resulting in an alkoxy radical, followed by a rearrangement, and subsequent sulfation of the epoxy group in the particle phase.

Chapter 7 deals with the structural characterization of MW 230, 214 and 170 organosulfates, which are present at a significant relative abundance in ambient PM_{2.5} aerosol relative to those of the isoprene-related MW 216 organosulfates. Evidence is presented that the unsaturated aldehydes 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal are BVOC precursors for the polar organosulfates with MWs of 230 and 214. These results complement those obtained in a previous study showing that the GLV 3-*Z*-hexenal serves as a precursor for MW 226 organosulfates. Thus, in addition to isoprene, the GLVs 2-*E*-hexenal and 3-*Z*-hexenal, emitted due to plant stress (mechanical wounding or insect attack), and 2-*E*-pentenal, a photolysis product of 3-*Z*-hexenal, should be taken into account for SOA and organosulfate formation. Extensive use was made of organic MS and detailed interpretation of the data (i.e., ion trap MS and accurate mass measurements) to elucidate the chemical structures of the MW 230, 214 and 170 organosulfates formed from 2-*E*-pentenal, and indirectly from 2-*E*-hexenal and 3-*Z*-hexenal. The MW 230 organosulfates were assigned to isomers of 3-sulfooxy-2,4-dihydroxypentanoic acid, the MW 214 organosulfates were attributed to isomers of 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid, and the MW 170 organosulfates were assigned to lactic acid sulfate and 1-sulfooxy-2-hydroxybutane. In addition, quantum chemical calculations were performed to explain the different MS behavior of the MW 214 organosulfates, where the isomer with the sulfate group at C-3 results in the loss of SO₃. The MW 214 and 230 organosulfates formed from 2-*E*-pentenal are explained by a pathway, which bears features of that proposed for the formation, in the presence of NO_x, of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from

methacrolein, which, as 2-*E*-pentenal, is also an α,β -unsaturated aldehyde. It is demonstrated that the MW 214 organosulfate, 2-sulfooxy-3-hydroxypentanoic acid, is unstable and readily carboxylates to form 1-sulfooxy-2-hydroxybutane, a MW 170 organosulfate. Furthermore, tentative evidence is obtained that lactic acid sulfate is generated from 2-*E*-pentenal.

It has been clearly shown in this work that the green leaf aldehydes 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal serve, as isoprene, as biogenic precursors for polar organosulfates. Their structures have been elucidated using mass spectrometric approaches; however, some of the proposed structures still need to be more firmly supported by, for example, organic synthesis. This is, for example, the case for the MW 212 organosulfates, discussed in Chapter 6, for which research is still ongoing and very recent experiments revealed that they originate from isoprene. Tentative formation pathways have been proposed in this work but additional research is warranted to support the proposed mechanisms. Furthermore, work in this field would also profit from improved chromatographic separation of polar organosulfates and quantitative determinations. Quantitation of organosulfates will allow to determine their relative contribution to the SOA mass and to establish under which atmospheric conditions and in which environments they are formed.

Samenvatting en besluit

Atmosferische aerosolen staan gekend als een van de meest belangrijke parameters die verschillende aspecten van onze planeet beïnvloeden, gaande van klimaatsverandering, luchtkwaliteit, zichtbaarheid, tot menselijke gezondheid. Teneinde hun rol in de chemie en de fysica van de atmosfeer en ons leven te kunnen voorspellen en te begrijpen is het nodig om inzicht te krijgen in hun bronnen, vormingsmechanismen, eigenschappen, en chemische samenstelling. Biogene vluchtige organische verbindingen (BVOCs) worden geëmitteerd door natuurlijke bronnen (bv. vegetatie) onder natuurlijke omstandigheden en als antwoord op stress, en zijn de belangrijkste precursoren voor atmosferische aerosolen, meer bepaald, secundair organisch aerosol (SOA), dit is organisch aerosol dat wordt gevormd door oxidatie van vluchtige organische verbindingen, zowel van natuurlijke als antropogene oorsprong, in de gas- en deeltjesfase. Dit doctoraat handelt voornamelijk over de structuurkarakterisering van polaire organosulfaten, BVOC oxidatieproducten die van atmosferisch belang zijn omdat ze hydrofiel zijn en als dusdanig wolkprocessen kunnen beïnvloeden. Organosulfaten hebben een gemengde biogene en antropogene oorsprong omdat ze worden gevormd in reacties van BVOCs of hun oxidatieproducten met zwavelzuur, dat zelf gevormd door oxidatie van zwaveldioxide dat van antropogene oorsprong is. Ze dragen ook bij tot de aerosolzuurtegraad door de aanwezigheid van de sulfaatgroep. Verschillende mechanismen leiden tot de vorming van organosulfaten in de deeltjesfase: (i) reactie van epoxy-bevattende SOA producten (bv. de met isopreen verwante C₅-epoxydiolen); (ii) opname van onverzadigde BVOCs (bv. methacroleïne, een gasfase-oxidatieproduct van isopreen) en reactie met het sulfooxy radicalair anion; en (iii) opname van tertiaire organonitraten (bv. organonitraten van de met isopreen verwante 2-methyltetrolen) en nucleofiele substitutie van de nitraat- door de sulfaatgroep. Er is veel informatie beschikbaar over SOA vorming uitgaande van terpenen en

isopreen, maar daarmee in tegenstelling is er weinig geweten over SOA vorming uitgaande van de “green leaf volatiles” (GLVs), die worden geëmitteerd als planten worden beschadigd of worden aangevallen door insecten. 3-*Z*-hexenal is een belangrijk GLV dat in het celmembraan wordt gevormd uitgaande van het onverzadigd vetzuur α -linolzuur door de inwerking van de enzymes lipoxygenase en hydroperoxide, en het wordt gedeeltelijk geïsommeriseerd tot 2-*E*-hexenal. Het C₅-onverzadigd aldehyde 2-*E*-pentenal is een gekend fotolyseproduct van 3-*Z*-hexenal.

Twee types aerosolmonsters werden onderzocht: enerzijds, gearchiveerde PM_{2.5} monsters, die werden geïncubeerd in K-puszta, Hongarije, een landelijke site met een gemengde vegetatie van loof- en naaldbomen, tijdens een 2006 zomerveldcampagne, en, anderzijds, SOA monsters die werden geproduceerd uitgaande van BVOCs, die dienst deden als precursoren voor de onderzochte organosulfaten, meer bepaald, de onverzadigde aldehyden 2-*E*-pentenal, 2-*E*-hexenal en 3-*Z*-hexenal. Ook werden referentie-organosulfaten verwant met het isopreen gasfase-oxidatieproduct methylvinylketon en met 2-*E*-pentenal bereid met behulp van respectievelijk, organische synthese en reactie met het sulfoxy radicalair anion. De structuurkarakterisering werd alleen uitgevoerd voor organosulfaten met een beduidende abundantie (relatief t.o.v. de met isopreen verwante C₅-epoxydiol organosulfaten) in PM_{2.5} omgevingsaërosol.

Voor wat betreft analytische methodologie, werd uitvoerig gebruik gemaakt van vloeistofchromatografie in combinatie met elektrospay ionisatie massaspectrometrie in de negatieve ionenmode [LC/(–)ESI-MS], meer bepaald, ionentrap tandem MS, hoge-resolutie MS, en gedetailleerde interpretatie van MS gegevens. Voor de chromatografische scheiding van polaire organosulfaten werd gebruik gemaakt van LC op een omgekeerde fase C₁₈ kolom met polaire retentie, alsook

van ionenparing LC op een omgekeerde fase C₁₈ kolom en dibutylammonium-acetaat (DBAA) als ionenparingsreagens. In een beperkt aantal gevallen werden ook kwantumchemische berekeningen uitgevoerd om inzicht te bekomen in het massaspectrometrisch gedrag van organosulfaten.

Deze thesis bevat drie inleidende hoofdstukken en vier hoofdstukken over specifieke studies, waarvan de drie eerste gepubliceerd zijn en de laatste een studie betreft die in druk is. De inleidende hoofdstukken (Hoofdstukken 1, 2 en 3) handelen over atmosferische aërosolen in het algemeen, doelstellingen van het onderzoek uitgevoerd in het kader van deze thesis, achtergrondinformatie over organosulfaten, en instrumentatie en methoden. De vier hoofdstukken met specifieke studies (Hoofdstukken 4, 5, 6 en 7) bespreken de structuurkarakterisering van nieuwe polaire organosulfaten, die verwant zijn met isopreen en de onverzadigde aldehyden, 2-*E*-hexenal, 3-*Z*-hexenal en 2-*E*-pental, alsook over de ontwikkeling van een ionenparing LC methode voor polaire organosulfaten.

Hoofdstuk 4 handelt over de structuurkarakterisering van een met isopreen verwant molecuulair gewicht (MW) 184 organosulfaat en de structuurrevisie van met isopreen verwante organosulfaten met MW 156, 170 en 200. Een belangrijke fractie van atmosferisch fijn stof bestaat uit organosulfaten, waarbij sommige van de meest polaire afkomstig zijn van de oxidatie van isopreen. De structuur van de ongekende polaire organosulfaten aanwezig in PM_{2.5} omgevingsaërosol werd gekarakteriseerd met behulp van LC/(–)ESI-MS, omvattende ionentrap MSⁿ en accurate massabepalingen, derivatizing van de carbonyl groep tot 2,4-dinitro-fenylhydrazones, en, in het geval van het MW 184 organosulfaat, vergelijking van de LC en MS karakteristieken met deze van gesynthetizeerde referentieverbindingen. De polaire organosulfaten met MW 156, 170, 184 en 200 werden gekarakteriseerd of bevestigd als sulfaatesters van glycolzuur (156), melkzuur

(170), 1,2-dihydroxy-3-butanon (184), glycolzuur glycolaat (200), 2-methyl-glycerinezuur (200) en 2,3-dihydroxybutaan-2-ol (200). Er werd een meer volledige structuurkarakterisering bereikt van polaire organosulfaten die worden gevormd uit isopreen. Een belangrijk resultaat was de karakterisering van een MW 184 organosulfaat dat verwant is met methylvinylketon, een abundant gasfase-oxidatieproduct van isopreen.

Hoofdstuk 5 handelt over de ontwikkeling van een ionenparingsmethode voor polaire, met isopreen verwante, organosulfaten, steunend op LC/(-)ESI-MS en gebruikmakend van een omgekeerde fase C₁₈ kolom en DBAA als ionenparingsreagens. In vergelijking met vroeger werk waarbij een omgekeerde fase C₁₈ kolom met polaire retentie werd gebruikt, kon een betere chromatografische resolutie worden bereikt voor met isopreen verwante polaire organosulfaten, zoals de sulfaatesters van de 2-methyltetrolen en 2-methyl-glycerinezuur, en bijgevolg een betere structuurkarakterisering. De beste resultaten werden bereikt door het ionenparingsreagens toe te voegen aan zowel de mobiele fase als de oplossing waarin de analieten werden heropgelost. Hierbij was de molaire overmaat van DBAA voor de testverbindingen (methaansulfaat, ethaansulfaat, 2-propaansulfaat en D-galactose-6-sulfaat) meer dan 103.

Hoofdstuk 6 handelt over de structuurkarakterisering van MW 226 en 212 organosulfaten, die een belangrijke abundantie hebben in PM_{2.5} omgevingsaërosol relatief t.o.v. de met isopreen verwante MW 216 organosulfaten. Er wordt aangetoond dat de GLV 3-Z-hexenal een precursor is voor biogeen SOA via de vorming van polaire MW 226 C₆-organosulfaten. De structuur van de MW 226 verbindingen werd gekarakteriseerd, alsook deze van structuurverwante MW 212 C₅-organosulfaten, waarvoor de biogene precursor nog ongekend is maar vermoedelijk verwant is met 3-Z-hexenal. De MW 226 verbindingen werden

toegewezen aan isomere sulfaatesters van 3,4-dihydroxyhex-5-eenzuur met de sulfaatgroep op de C-3 of C-4 posities (nl. 3-sulfooxy-4-hydroxyhex-5-eenzuur en 4-sulfooxy-3-hydroxyhex-5-eenzuur). Twee MW 212 verbindingen werden toegewezen aan isomere sulfaatesters van 2,3-dihydroxypent-4-eenzuur, waarvan er twee gesulfateerd zijn op de C-3 positie en een op de C-2 positie. De vorming van de MW 226 organosulfaten wordt tentatief verklaard door foto-oxidatie van 3-Z-hexenal in de gasfase met tussenkomst van een alkoxyradicaal, gevolgd door een omlegging met vorming van een epoxygroep, en sulfatering van de epoxygroep met zwavelzuur in de deeltjesfase.

Hoofdstuk 7 handelt over de structuurkarakterisering van MW 230, 214 en 170 organosulfaten, die een belangrijk abundantie hebben in PM_{2.5} omgevingsaërosol relatief t.o.v. de met isopreen verwante MW 216 organosulfaten. Er wordt aangetoond dat de onverzadigde aldehyden 2-*E*-pental, 2-*E*-hexenal en 3-*Z*-hexenal BVOC precursoren zijn voor de polaire organosulfaten met MW 230 en 214. Deze resultaten zijn complementair met deze bekomen in een vorige studie (Hoofdstuk 6) waarbij aangetoond werd dat de GLV 3-*Z*-hexenal een precursor is voor MW 226 organosulfaten. Dus, naast isopreen moeten ook de GLVs 2-*E*-hexenal en 3-*Z*-hexenal, die worden geëmitteerd als gevolg van plantenstress (mechanische verwonding en insectenaanvallen), en 2-*E*-pental, een fotolyse-product van 3-*Z*-hexenal, in aanmerking worden genomen voor SOA en organosulfaatvorming. De chemische structuren van de MW 230, 214 en 170 organosulfaten gevormd uitgaande van 2-*E*-pental (en indirect ook uitgaande van 2-*E*-hexenal en 3-*Z*-hexenal) werden gekarakteriseerd met organische MS (nl. ionentrap MS en accurate massabepaling) en gedetailleerde interpretatie van de MS gegevens. De MW 230 organosulfaten werden toegewezen aan isomeren van 3-sulfooxy-2,4-dihydroxypentaaanzuur, de MW 214 organosulfaten aan isomeren van 2-sulfooxy-3-hydroxypentaaanzuur en 3-sulfooxy-2-hydroxypentaaanzuur, en de

MW 170 organosulfaten aan sulfaatesters van melkzuur en 1-sulfooxy-2-hydroxybutaan. Ook werden kwantumchemische berekeningen uitgevoerd om het verschillend MS gedrag te verklaren van de MW 214 organosulfaten, waarbij het isomeer met de sulfaatgroep op C-3 resulteert in het verlies van SO_3 . De vorming van de MW 214 en 230 organosulfaten uitgaande van 2-*E*-pentenal wordt tentatief verklaard met een route, die stappen bevat van deze voorgesteld voor de vorming, in aanwezigheid van NO_x , van 3-sulfooxy-2-hydroxy-2-methylpropaanzuur uitgaande van methacroleïne, dat zoals 2-*E*-pentenal ook een α,β -onverzadigd aldehyde is. Er werd aangetoond dat het MW 214 organosulfaat, 2-sulfooxy-3-hydroxypentaanzuur, onstabiel is en decarboxyleert met vorming van 1-sulfooxy-2-hydroxybutaan, een MW 170 organosulfaat. Verder kon worden aangetoond dat de sulfaatester van melkzuur wordt gevormd uitgaande van 2-*E*-pentenal.

Er kon duidelijk worden aangetoond in dit werk dat de onverzadigde aldehyden, 2-*E*-pentenal, 2-*E*-hexenal en 3-*Z*-hexenal, zoals isopreen fungeren als biogene precursoren voor polaire organosulfaten. De structuren werden gekarakteriseerd met behulp van massaspectrometrische methoden; voor sommige ervan moeten de voorgestelde structuren nog worden bevestigd met een andere methode, zoals bv. organische synthese. Dit is bijvoorbeeld het geval voor de MW 212 organosulfaten, die worden besproken in Hoofdstuk 6, en waarvoor onderzoek nog lopend is en recente experimenten aantonen dat ze worden gevormd uitgaande van isopreen. Tentatieve vormingsroutes werden voorgesteld maar verdere studies zijn wenselijk om deze te bevestigen. Verder zou onderzoek over polaire organosulfaten ook worden bevorderd door een verbeterde chromatografische scheiding en kwantitatieve bepaling. Deze laatste moet toelaten om meer nauwkeurig hun relatieve bijdrage tot de SOA massa te berekenen en te bepalen onder welke atmosferische omstandigheden en in welke omgeving ze worden gevormd.

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